THE JOURNAL

—OF THE—

AMERICAN CHEMICAL SOCIETY.

VOLUME XVIII.

1896.

COMMITTEE ON PAPERS AND PUBLICATIONS:

EDWARD HART, Editor,

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EASTON, PA.:
CHEMICAL PUBLISHING CO.
1896.

Contents of Vol. XVIII, 1896.

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VOL. XVIII. [JANUARY, 1896.] NO. 1.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

ON THE DETERMINATION OF CARBON DIOXIDE BY ABSORPTION.

BY H. HEIDENHAIN.

Received October 19, 1895.

OF all the methods for the determination of carbon dioxide the absorption method is the most reliable and most correct. It is, however, not easy to obtain good results with an absorption apparatus. The inexperienced generally get varying results; after some practice the results become uniform, but either always too high or too low. The application of a corresponding correction may be used with advantage in such cases, but one must admit that this is a makeshift only. As long as the causes of the excesses or shortages are unknown, the influence of such causes cannot be estimated, and therefore one is always uncertain whether the applied correction actually compensates the error.

I therefore decided to seek the causes. If I could not remove them, I would at least measure their influence. The correction which was so far found by merely empirical methods could then be calculated from the obtained data. Thus the method would be brought beyond dispute, at least from the scientific standpoint.

The method and the apparatus which I shall discuss in the following are those described by Fresinius.[1] Before going into details, I may briefly remind the reader of them. The carbon

[1] Quant. Anal. I, page 449, and II, page 308.

dioxide is developed by boiling with a dilute acid. A mixture of carbon dioxide, air and water vapor is generated, from which the latter is removed first. From the remaining gas mixture carbon dioxide is absorbed. These operations are performed by a current of air free from carbon dioxide. Consequently the apparatus has to provide for

(1) an air purifying device,
(2) a developing apparatus,
(3) a drying apparatus,
(4) an absorption apparatus,
(5) an aspirator.

Each of these parts must do its work perfectly, if good results are to be obtained. This can be easily accomplished as to the air purifying and the drying apparatus by making them amply large. The evolution flask can be rather small with substances which do not foam, but with foaming substances like baking powder the size of the flask must be chosen according to the practical requirements. For our work a capacity of 300 cc. is sufficient.

The absorption apparatus occasions some difficulty. Its size is limited by the capacity of the analytical scale. We use U-tubes filled with soda-lime and calcium chloride as recommended by Fresenius. My experience is that these tubes contain generally too little calcium chloride, whereby losses are caused. Soda-lime loses some moisture in a current of air dried by calcium chloride. In order to retain the moisture a considerable length of calcium chloride must be provided at the end of the second U- tube. Fresenius prepares both tubes alike and exchanges them after the first use in order to have the fresher filling in front the second time. I do not think that this is the best plan. My opinion is that each tube has to serve a particular purpose, and should consequently have a special outfit. In the first tube carbon dioxide is to be absorbed and therefore it must be filled mainly with soda-lime. The second tube has to answer two different requirements. Firstly it has to act as a safety tube to catch any residue of carbon dioxide not absorbed in the first tube. It is considered that these traces naturally are in a highly dilute state, it seems indispensable that in order to

retain them with safety a powerful absorbent must be employed, in other words, a fresh filling. Secondly it has to absorb the moisture which during the operation has been given off by the soda-lime in both tubes. This can be attained only if the current of air passes a rather long column of calcium chloride before leaving the tube. To meet these requirements the second tube is filled half with soda-lime and half with calcium chloride.

As already mentioned, the first absorption tube receives mainly a filling of soda-lime. Only at the end at which the current of air enters a layer of calcium chloride is provided in order to absorb any moisture which may rise from the soda-lime in this direction.

This manner of filling the two absorption tubes has proved very satisfactory. Experience teaches very soon how much carbon dioxide can be absorbed by the first tube with safety and how often the filling must be renewed. We found that with our soda-lime twenty grams of filling can take up one gram of carbon dioxide. The filling of the second tube, which consists of about ten grams of soda-lime and ten grams of calcium chloride, needs renewing but seldom. As we work its weight increases at each determination very constantly by about five milligrams, whether the quantity of carbon dioxide be large or small or a blank determination be made. This proves that the small increase is caused entirely or almost entirely by moisture. When after repeated use the total increase amounts to about two-tenths gram it is observed that the increase diminishes and at the same time the results are low. Therefore we renew the filling as soon as the total increase amounts to one-tenth gram.

The aspirator is another part to which in my opinion not enough attention is paid. As will be shown later in this article, the aspirator must allow a perfect regulation of the air current and must show the quantity of air used. Both are easily attained by employing a Mariotte's bottle.

As to the manner in which the method is to be carried out, the following points seem to be worth noting. It is evident that the current of air must not exceed a certain rapidity if the absorption is to be complete in all parts of the apparatus. As the absorption of carbon dioxide by soda-lime takes place according

to general experience very easily and quickly, there is practically no danger of loss. Long columns of calcium chloride in the drying tubes secure proper absorption of moisture in this part. It remains only to make the absorption of moisture in the second weighed tube perfect. In my opinion it is impossible to give on this point any definite rules which can be followed in all cases. On the contrary the maximum rapidity admissible must be found by experiments, not only for each apparatus but also for each new lot of absorbents, as especially the commercial soda-lime has a varying content of moisture.

In order to find the allowable rapidity of the air-current one may proceed practically as follows: The apparatus is charged exactly as for an analysis except that the carbonate is left out; in other words, a blank experiment is made. The aspiration is started with a rapidity of fifty cubic centimeters per minute. After two liters of air have passed it is interrupted. If the absorption tubes show a loss in weight the experiment must be repeated with less rapidity, say forty cc. per minute, and in this manner must be continued until the weight of the tubes is constant. If the work has been done with due precaution it will now be found that the first tube has lost just as much as the second has gained. If this is not the case it is a sure indication that the result is due to a compensation of errors.

The ascertained maximum of rapidity of the air-current must not be exceeded in determinations; a slower rate is unobjectionable. It may be mentioned here that the calcium chloride in the second tube must be of the same quality as that in the drying apparatus, which is also evident from the remarks made by Fresenius.[1]

Further it is manifest that a certain quantity of air must be aspirated in order to transfer all carbon dioxide from the evolution flask and the drying apparatus to the absorption tubes. The common directions on this point, as for instance two air-bubbles a second for half an hour, and similar rules, are too indefinite, and in fact do not suffice. On the contrary the required quantity of air must be determined for each apparatus. This is done simply by liberating about a half gram carbon

[1] Quant. Anal., I, 72.

dioxide in the evolution flask, aspirating a certain quantity of air, for instance one-half liter, weighing the tubes and repeating the aspiration until the weight of the tubes remains constant. As a precautionary measure some addition is to be made to the minimum thus found.

In order to regulate the current of air and to keep it constant some skill is required. The aspirator must not be put in operation before the air in the apparatus comes to equilibrium, which generally is the case after the liquid in the evolution flask has boiled a few minutes. The flame is then reduced just far enough to keep the liquid slightly boiling. Now the aspirator is connected and the water allowed to run off until it comes to a standstill. Now is the time to open the cock between the evolution flask and the air purifying apparatus. Immediately the outflow from the aspirator starts and becomes constant after a few seconds. By aid of watch and measuring cylinder the speed is soon regulated.

We make it a rule to aspirate with but half the allowable rapidity until the main quantity of carbon dioxide is absorbed, *i. e.*, until the soda-lime tube has recooled : from then to the end of the operation the full speed is used. It may be said that in our work these speeds are respectively ten cc. and twenty cc. per minute.

The flame remains burning during the whole time of aspiration. If the flame were extinguished the air in the evolution flask would cool and contract, making a regulation of the air-current impossible.

Another point often overlooked is the presence of carbon dioxide in distilled water and laboratory air. There is too much in both to neglect. The whole apparatus, including the evolution flask, must be filled with air free from carbon dioxide and the distilled water must be freed from it by boiling with a little acid. In pouring the water into the evolution flask air must not be allowed to enter.

Finally, corrections for changes of temperature and air-pressure are indispensable, as the tubes and their contents occupy a rather large volume.

In regard to accuracy of our results little remains to be desired. Blank determinations give a gain or loss of not more

than two-tenths mg., and determinations of carbon dioxide in clear crystals of Iceland spar give, if one gram is employed, results which vary from 44.01 to 43.96 per cent. The explanation for these slight variations may be found partly in the inexactness of the weighings, of which four must be made for every determination, and partly in the quantity of moisture condensed on the surface of the tubes, which varies according to the moisture in the surrounding air.

It may be well to append a sketch of the apparatus as modified by me. Great care has been taken to draw all parts in proper proportion. The ratio is 1 : 12.

Some explanations in regard to details may follow:

a. Air-purifying cylinder, filled with soda-lime. At the top is cotton to keep back soda-lime dust.

b. Cock to regulate the air-current.

c. Capillary tube to offer resistance to the air current in case cock *b* is opened too far.

d. Funnel tube, closed at the bottom by a perforated rubber stopper into which

e. A glass tube is fitted. This arrangement, in connection with cock *b*, is a substitute for a three-way cock, but has the advantage that the regulating part, *i. e.*, "*b*" does not become wet and is not exposed to heat.

f. Evolution flask.

g. Cooler. Consists of a glass tube around which a lead pipe is wound. It was adopted by us on account of varying water pressure. It stands sudden changes of pressure very well.

h. Drying tube filled with coarse calcium chloride.

i. A little pumice stone prepared with copper sulphate.

k. Drying tube filled with fine carcium chloride.

l. Cock to close drying apparatus when not in use.

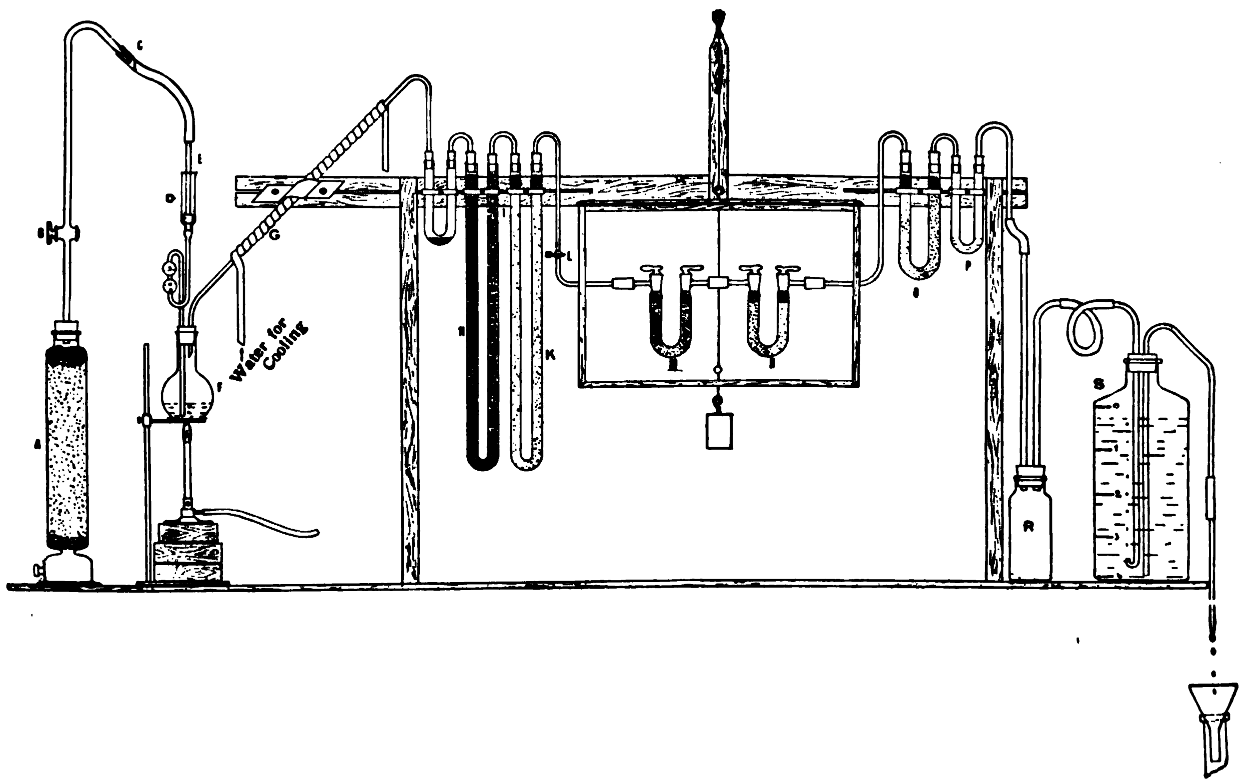
m and *n*. Absorption tubes, filled as described above. They are put in a glass case to protect them from dust. The connections are made by perforated rubber stoppers.

o. Guard tube, containing calcium chloride and soda-lime.

p. Indicator tube.

r. Safety bottle, to receive water which may be sucked back from

s. The aspirator.



Improved Apparatus for Carbon Dioxide.

THE NATURAL OXYCELLULOSES.

By C. F. Cross, E. J. Bevan and C. Beadle.

Received October 10, 1895.

IN a previous short communication[1] we dealt with a controversial point which had arisen in regard to the constitution of the furfural-yielding constituents of plant-tissues. What there has been at issue between de Chalmot and ourselves in this matter, is at least clearly stated, and we have been engaged in accumulating experimental material as a further contribution to the solution of an important question in the chemistry of tissue-formation, which cannot usefully be further discussed *a priori*.

In this investigation we have been ably assisted by our friend Mr. Claude Smith, who has carried out the whole of the laboratory work, and Dr. Voelcker, the well known chemist of the Royal Agricultural Society, who has kindly cooperated with us in placing his laboratory at our disposal and supplying material for the investigation.

In the first instance we have traced the history of selected crops of barley, in relation to the elaboration of "furfuroids," to use a convenient short description of these characteristic furfural-yielding constituents.

The crops selected were grown upon two of the experimental plots of the Royal Agricultural Society's station at Woburn, (England):

Plot 1 representing a soil permanently unmanured and growing barley continuously.

Plot 6[2] on the other hand is manured with the maximum of fertilizers and gives continously the maximum yield of straw and grain.

These plots represent therefore the extreme conditions of growth, unfavorable and favorable.

The plants were harvested at intervals of one month and investigated according to the subjoined scheme:

(1) The "total furfural," obtained by "distilling" the entire plants with hydrochloric acid, was determined.

(2) The plants were treated for the elimination of pentosans

[1] This Journal, 17, 286.

[2] Manured with potassium, sodium and magnesium sulphates, calcium superphosphate and sodium nitrate.

and generally, of constituents not belonging to "permanent tissue," as follows:

(*a*) Exhaustive treatment with boiling alcohol; (*b*) Digestion in alkaline solution of one and one-half per cent. sodium hydroxide for some hours, followed by washing, first cold, lastly at the boiling temperature; (*c*) Digestion in dilute one and one-half per cent. hydrochloric acid for some hours, followed as before, by cold and hot washings. The product of these treatments may be taken as fairly representing the cellular tissue of the plant *less* the cell-contents, and may be described as permanent tissue. This description we admit is somewhat arbitrary, but it will be conceded that the residue from the treatments above described its free from pentosans and all the more readily hydrolyzable constituents of the growing plant.

It is not necessary to reproduce minutely the experimental details of the investigation. It is sufficient to state that the results were in all cases controlled by duplicate experiments.

Date.	Age of crops.	Plot.	Total dry weight in per cent.	Furfural per cent. of dry weight. (*a*)	Permanent tissue per cent. of total.	Furfural from permanent tissue. Per cent. tissue. (*b*)	original. (*c*)	ratio. *a* : *c*
May 7	6 weeks	1	19.4	7.0	53.4	12.7	6.8	1.03 : 1
		6	14.7	7.0	55.9	12.3	5.8	1.20 : 1
June 4	10 weeks	1	17.6	7.7	52.9	11.6	6.1	1.26 : 1
		6	13.5	8.1	58.5	13.4	7.8	1.04 : 1
July 10	15 weeks	1	42.0	9.0	65.7	9.8	6.4	1.40 : 1
		6	32.9	10.6	65.7	12.5	8.2	1.30 : 1
August 21	21 weeks	1	64.0	11.9	70.0	14.5	10.1	1.17 : 1
		6	64.6	13.4	70.5	15.0	10.6	1.26 : 1
August 31[1]	22 weeks 3 days	1	84.0	12.6	75.0	16.5	12.4	1.02 : 1
		6	86.4	12.4	78.4	15.1	11.8	1.05 : 1

With regard to the distribution of the furfuroids in the plant the following determinations were made in specimens taken from plot 6, on July 18, the crop being sixteen weeks old:

	Whole plant (moist). Per cent.	Whole plant (dry) Per cent.
Stems	50.0	41.7
Leaves	15.3	19.6
Ears	34.6	38.6

1 The samples taken on August 31st were *after* the crops were harvested.

	Dry matter. Per cent.	Ash, dry matter. Per cent.	Permanent tissue. Per cent.	Furfural gross.	Furfural in permanent tissue.
Stems	32.6	4.0	76.6	9.5	12.2
Leaves	50.1	7.0	49.7	12.1	16.0
Ears	44.2	7.0	79.0	7.5	9.6

It appears from these results that the leaves contain a large proportion of the easily hydrolyzable furfuroids, *e. g.*, pentosans; those of the stems and ears, on the other hand, are for the most part in the more resistant form of tissue-furfuroids. The higher proportion of furfuroids in the leaves may be taken as correlated with the special assimilating functions and more active oxidizing conditions obtaining in these organs, and as indicating that furfuroids of lower molecular weight may be assimulated or elaborated to permanent tissue. The probability of this must in fact be admitted. For although de Chalmot's experiments[1] contradict the hypothesis that the pentoses are so elaborated, the problem as regards oxidized hexose derivative can hardly be considered as having been seriously attacked.

The investigations of these barley plots are being continued during the current year, with special attention to the more positive indications of the above results. The following are the results of the examination of specimens taken on May 15, the crop being seven weeks old; the figures represent percentages;

	Plot 1.	Plot 6.
Total dry matter	20.6	17.8
Ash of dry matter	13.7	18.0
Nitrogen of dry matter	3.65	3.87
Alcoholic extract	19.0	23.8
Nitrogen of alcoholic extract	2.5	2.8
Permanent tissue	53.9	56.7
Ash of permanent tissue	3.8	4.0
Nitrogen of permanent tissue	4.2	4.5

The furfural numbers calculated on the dry ash-free products are as follows:

	Furfural gross. Per cent. (*a*)	Furfural in permanent tissue. Per cent. of tissue. (*b*)	Furfural in permanent tissue. Per cent. of original. (*c*)	Ratio. *a* : *c*
Plot 1	7.6	10.6	5.50	1.40 : 1
Plot 6	7.1	10.0	5.44	1.12 : 1

[1] This Journal, 16, 618.

These numbers confirm those of the 1894 crops in their general bearings. The season, however, has been so far very different, the week preceding the 15th being cloudless with high summer temperature, as against a cold wet week in the corresponding period of 1894. The higher ratio $a : c$ accords with the higher rate of assimilating obtaining under such conditions.

The more extensive scale of the investigation has reference to a more strictly physiological scheme of observation to be made at the critical period of growth, *viz.*, flowering, fruiting, and ripening of the grain. These numbers lead to the following conclusions :

1. The "permanent tissue" (cellulose) of the cereals contains *ab initio*, a large proportion of oxidized groups, *i. e.*, oxycelluloses.

2. The furfuroids of the cereals (Haulm) are localized mainly in the cell-substance, in the earlier and later stages of growth, in fact, almost exclusively. Towards the period of most active growth the proportion of tissue furfuroids falls from ninety to seventy-five per cent. of the total.

3. Increasing again during the period of maturation indicates that the furfuroids of what may be termed the lower grade are assimilated to the more resistant, or cellulose, form.

4. Extreme variations of the soil-conditions, *i. e.*, supply of inorganic nutrient material—is without effect upon the permanent tissue in the earlier and later stages of growth, but determines some variations of the proportion of tissue furfuroids in the intermediate states.

5. The results show that the composition of the permanent tissue is a constant of the plant, and largely independent of the particular conditions of cultivation. This latter result is confirmed by the result of a similar investigation of barley straws from the Rothamsted Experimental Station. Specimens of the fully matured straws grown upon plots selected as showing extreme variations of the conditions of cultivation, gave the following results :

	Plot.	Total furfural per cent.	Permanent tissue per cent.	Furfural in permanent tissue per cent. of tissue.	of straw.
Minimum fertilization.	1.*O*	14.5	72.4	15.8	11.4
	3.*O*	15.5	72.4	14.7	10.6
	6_1.	15.8	72.6	15.8	11.5
Maximum fertilization	4*A.A.S.*	12.4	76.4	16.2	12.4
	4*AA.*	15.1	80.2	16.0	12.8
	7_2.	15.0	82.3	14.1	11.6

The following are the conditions of fertilization:

Plots 1. *O.* and 6_1, were unmanured continuously.

Plot 3. *O.*, manured with sodium, potassium, and magnesium sulphates.

Plot 4 *A.A.S.*, manured with sodium nitrate, sodium silicate, calcium superphosphate and sodium potassium, and magnesium sulphates.

Plot 7_2, fourteen tons farm-yard manure.

Plot 4 *A.A.*, potassium, sodium, and magnesium sulphate, calcium superphospate, and sodium nitrate.

These results are from an agricultural point of view of negative value. It was *a priori* possible that the composition of the permanent tissue would have varied with the prevailing conditions of assimilation. Such variations are not discoverable in the furfural-constants of the products, which express their most characteristic constitutional features. Physiologically, on the other hand, the results are of more positive bearing on the processes of assimilation, showing that these are in an important sense invariable.

It might be assumed in a superficial view that this conclusion was obvious *a priori*, and the experimental verification therefore gratuitous. On reflection, however, it will be conceded: (1) that we have not long been in possession of quantitative methods of diagnosing the constitutional features of the components of plant tissues—celluloses, oxycelluloses, lignocelluloses, etc., —and (2) that, whatever the probability, the point is not specifically dealt with in works in plant-physiology.[1]

It is a point which we have dealt with before in regard to the typical lignocellulose, the jute fiber. In an investigation of the

[1] The current views on the subject of lignification and thickening of cell walls, imply that the permanent tissue in its earliest phases invariably consists of a pure (normal) cellulose. The chemist has to remember that the morphologist attaches no specialized significance to the term cellulose.

growth of the plant under the artificial conditions of "hot-house cultivation," Mr. A. Pears obtained the bast fiber, showing considerable divergence on ultimate analysis (C : H : O) from the normal Indian product, but with identical constitutional features. The low carbon percentage of the product was shown to be due to "dilution" by water of hydration ; dehydration had not proceeded as far as obtained under the normal conditions of growth ; but in all essential respects the quantitative chemical features of lignification were unaffected.[1] The point is therefore established in regard to two main types of tissue-formation.

Reverting now to the history of tissue-formation in barley plant.

In reference to the germination process, we commenced observations[2] upon the earliest stages of tissue-formation in regard to the formation and fixation of furfuroids, but, recognizing the prior claims of de Chalmot in this field of investigation, we are satisfied to leave the subject in such good hands, merely noting that we have joined issue with him in regard to the interpretation of the furfural-constants.

De Chalmot has especially investigated the influence of the two factors which might be expected to affect the formation and elaboration of these furfuroids, *viz.*, (1) light; (2) the supply of nitrogen (nitrate). Light was found to be without effect in these earlier stages of growth; and with a liberal supply of nitrates the amount of furfuroids in the young plants was found not to decrease. These results again point to the invariable habit of the cell in regard to the formation of tissue.

We have endeavored to produce a still more drastic variation of the conditions of assimilation, as follows: Young plants of oats seven weeks old were placed in the following solutions: (*a*) water; (*b*) dilute nitric acid of 0.25 per cent.; (*c*) of one half per cent.: (*d*) of one per cent. The plants withered only gradually. After about ten days they were removed, dried and investigated. The results are given below:

Twenty plants before experiment weighed 25.8 grams and contained 16.7 per cent. dry matter.

Twenty plants in water (*a*) weighed 39.0 grams and contained 10.2 per cent. dry matter.

[1] *J. Chem. Soc.*, *1893*, 967; Cross & Bevan: "Cellulose," pages 111-113.
[2] *Ber. d. chem. Ges.*, 27, 1061.

Twenty plants in dilute acid (*b*) weighed 18.0 grams and contained 21.3 per cent. dry matter.

Twenty plants in dilute acid (*c*) weighed 15.0 grams and contained 24.4 per cent. dry matter.

Twenty plants in dilute acid (*d*) weighed 13.0 grams and contained 31.0 per cent. dry matter.

From the dry matter the following percentages of furfural were obtained :

(*a*)	(*b*)	(*c*)	(*d*)
8.2	9.2	8.2	8.5

The uniformity of these numbers is curiously at variance with the extreme variations of the conditions of retrograde development, which are apparent from the statistics of the relative weights of these plants.

In a second series of experiments very different results were obtained. In this case the plants were taken at a more advanced stage of growth—thirteen weeks old. They were placed in water and dilute solutions of nitric acid, respectively, as before, remaining for ten days, when they showed signs of withering. They were removed, dried and analyzed for "total furfural," with the following results :

	Cultivations in water, per cent.	Dilute nitric acid, per cent.		
		0.25	0.50	1.00
Furfural	4.6	4.9	5.9	7.8

These variations determined by artificial treatment may appear out of harmony with the invariability of the results obtained in the first series. It will be noted, however, that the oats show a very different initial proportion of furfuroids, and appear to contain carbohydrates susceptible of attack by nitric acid.

The more advanced period of growth (thirteen weeks) at which the plants were taken, has been previously shown to be one of maximum normal variation of the furfuroids, which is consistent with maximum variations under retrograde development, and we may in future experiments follow the indications of these observations, that the most active period of growth offers the most favorable conditions for the study of variations artificially determined.

The purpose of the present investigations being to accumulate

experimental material the observations were extended to products of widely different origin, life-history, or formation. Subjoined are the numbers obtained with (*a*) mangels, and (*b*) gooseberries :

(*a*) Long red mangels were taken at intervals from a selected field, and the furfural and other constants determined, as follows:

Date.	Average wt. per root.	Dry matter per cent.	Ash of dry matter per cent.	Permanent tissue per cent.	Furfural whole root. (dry) per cent.	Furfural permanent tissue (dry) per cent.
June 30	1.5	12.7	11.0	25.3	4.1	12.6
August 6	300.0	11.5	12.0	28.8	4.3	11.4
October 11	1456.0	13.1	7.8	14.9	3.7	11.4

The furfural numbers, it will be remarked, are uniform over the whole period of growth. The proportion of furfuroids moreover is small, and further investigation of this group of products from our present point of view is therefore abandoned.

(*b*) The berries were examined at an interval of one month, with the following results:

Date.	Dry matter per cent.	Permanent tissue per cent.	Furfural whole fruit per cent.	Furfural permanent tissue per cent.
May 16	9.2	21.5	4.8	7.8
June 17	9.1	23.5	3.9	7.2

These numbers again are devoid of any characteristic such as invite further investigation. Other typical products were also examined with similar results. So far, therefore, the selection of the cereals as the typical case of the elaboration of cellulose-tissue with a maximum of furfuroid constituents is justified.

As we have before indicated it is not the purpose of the present communication to attempt any final conclusions as to the bearings of these results upon the general questions of assimilation and metabolism. We may perhaps again insist on the one prominent result of these investigations, which is to establish the uniform characteristic and uniform distribution of the furfuroids of the cereal straw throughout its substance :

(1) The entire straw in the matured state is characterized by yielding twelve to fifteen per cent. furfural; and (2) the "cellulose" isolated from the straw by the severe handling of the paper-maker ; *viz.*, digestion with caustic lye (two to three per

cent. sodium hydroxide) at elevated temperatures (forty to sixty pounds steam pressure), is identically characterized, yielding twelve to fifteen per cent. furfural on boiling with condensing acids.

This uniformity of distribution and uniformity of resistance to alkaline hydrolytic treatment of the widest range, establishes the molecular homogeneity of the tissue-substance in regard to the relative proportion of furfuroids to normal hexose groups. The results of our investigations of the history of the formation of the tissue are strictly correlative, and the elaboration of products of such characteristics must be regarded as an essential and primary property of the unit cell, in the same sense that alcoholic fermentation is a property of the yeast cell. To put it perhaps more directly: the constitution of assimilated material in the plant is immediately determined by the molecular configuration of the assimilating material. This view has been expressly formulated by E. Fischer[1] in reference to the origin of the carbohydrates in the plant. The more evidence we have that the assimilating process remains invariable in its products, notwithstanding wide variations in the external conditions, the more necessary does it become to regard the essential *directive* factors of the process as material, *i. e.*, as residing in the material configuration of the cell rather than determined by external forces. The results of our investigations contribute to the establishment of this view.

PART II.

I. THE CONSTITUTION OF THE CEREAL CELLULOSES.

We have made some progress in the isolation of the "furfuroid" constituents of celluloses. The more important differences which they exhibit from the normal celluloses we have dealt with in previous papers.[2] Although they are not resolved by alkaline hydrolysis we have found certain reagents which determine a satisfactorily sharp separation of their furfural-yielding component groups. Thus:

(*a*) Pure bleached straw-cellulose was treated with sulphuric acid at 1.62 specific gravity; the cellulose dissolves to a nearly

[1] *Ber. d. chem. Ges.*, **27**, 3231.
[2] *Ber. d. chem. Ges.*, **27**, 1061; C. Smith, *J. Chem. Soc.*, **65**, 473.

colorless solution. After standing some time (three hours from the start) the solution was poured into water. The white gelatinous precipitate of cellulose (hydrate) was filtered off and exhaustively washed, dried, and weighed. It amounted to sixty-four per cent. of the original. The reprecipitated cellulose and the filtrate were both distilled for elimination of furfural; the proportions obtained, calculated on the original cellulose, were:

	Furfural. Per cent.
Reprecipitated cellulose	0.6
Products soluble on dilution	14.0

The "furfuroids" therefore are hydrolyzed to soluble derivatives by the process.

(*b*) A second specimen was dissolved by heating with a concentrated solution of zinc chloride, the viscous solution poured into water, and the precipitate filtered off. Similar determinations were made as in (*a*), with the following results:

	Furfural (calculated on original cellulose). Per cent.
Reprecipitated cellulose	0.9
Product soluble on dilution	10.4

It is to be noted that furfural is freely formed in the process of heating with the concentrated solution of zinc chloride, and some quantity is volatilized. The reprecipitated cellulose (hydrate) has the characteristic of the normal celluloses. On combustion of these products the subjoined numbers were obtained:

Carbon	43.00	43.07
Hydrogen	7.14	6.99

corresponding with the formula $3C_6H_{10}O_5.H_2O$.

The products in solution in the acid liquid would appear to be capable of isolation by simple means, *viz.*, by neutralizing with barium carbonate, filtering, and evaporating.

Being derivatives of unknown constitution it was deemed advisable to prepare them in large quantity, and we proceeded to carry out the above process of hydrolysis on the scale of 100 grams per operation, as preliminary to working on the still larger scale of kilograms.

Proceeding as described we have obtained, on evaporating the filtrate from the barium sulphate, a light-colored gum resembling dextrin.

The first preparation gave, on distillation with hydrochloric acid, only eight and two-tenths per cent. of its weight of furfural; whereas, had we succeeded in obtaining the furfuroids only, as in the experiments on the smaller scale, the products should have yielded forty to fifty per cent.[1]

On reverting to the small scale we obtained this result:

Two grams of the cellulose being dissolved and the solution diluted and filtered from the reprecipitated cellulose; the filtrate was boiled with barium carbonate, filtered, and made up to 200 cc. Of this solution, eighty cc., on evaporation, gave 0.144 gram organic solids; a second, eighty cc., distilled for furfural, gave an amount correspondidg to 46.6 per cent. of the weight of the organic solids.

On further investigation of the products obtained on the large scale we found a large proportion retained as an insoluble barium compound. On boiling the washed precipitate with ammonia it yielded an extract, which on drying and "distilling" with hydrochloric acid, gave 12.5 per cent. furfural. It appears, therefore, that the products are resolved into three groups:

1. Normal cellulose (hydrate) reprecipitated, on dilution.

2. Soluble in water, but combining with barium carbonate to form insoluble compounds.

3. Soluble in water, but neutral, in properties, and therefore forming no barium compounds.

It appears also that the discrepancies between the results on the small and on the large scale are due to the conditions affecting group 2. These conditions are being carefully studied with the view of controlling the operation on the large scale. We have further characterized the soluble products of the hydrolysis as obtained on the small scale under most favorable conditions, as follows:

(*a*) *Copper-oxide reduction*.—As first obtained in solution the reduction equivalent, referred to that of dextrose as 100, has been

[1] Unless we assume that the configuration of the products is changed by the process of solution in sulphuric acid, which is not an improbable hypothesis. See *J. Chem. Soc.*, 65, 477.

determined at 30.6 After further hydrolyzing by boiling in the solution diluted to contain two per cent. sulphuric acid, it reached a maximum at 68.3

(*b*) *Osazone.*—After hydrolysis to this maximum the products were treated with phenylhydrazine under the usual conditions of formation of osazones. A characteristic product was obtained crystallizing well from solution in benzene. It was found to melt at 154°. On analysis it gave a quantity of ammonia corresponding to eight and four-tenths per cent. nitrogen. The parent substance is still, therefore, a product of relatively high molecular weight, approximately of the dimensions C_{16} to C_{18}, or, more strictly, containing one reactive CO group in the unit of these dimensions.

(*c*) *Decomposition by oxidants.*—On treatment with potassium permanganate in neutral solution it gives large yields of acetic acid. The products of oxidation by Fehling's solution also contain a large proportion of this acid.

(*d*) *Acetylation.*—The two products of hydrolysis not yet having been isolated on the large scale, the reaction with acetic anhydride has been studied with the parent substance. These celluloses contain reactive hydrolysis groups, forming an acetate on digestion with the anhydride at its boiling-point. The yield obtained in one experiment was 124 per cent. The product being insoluble in and unaffected by the usual solvents of the cellulose acetates, it was possible that a more complicated reaction had resulted, *e. g.*, condensation of the furfuroids to furfural and union with the anhydride to furfuracrylic acid. On distillation with hydrochloric acid the product yielded nine and a half per cent. furfural, which amounts to twelve per cent. of the original cellulose. The reaction will be further investigated with the isolated furfuroids.

(*e*) *Qualitative Reactions.*—The cereal-celluloses, as we have frequently stated, do not give the reactions characteristic of the pentosans, nor do the soluble products of acid hydrolysis obtained as described.

The celluloses on the other hand give a rose-red coloration on boiling with solutions of aniline salts, and the reaction is also obtained with the products of hydrolysis. From the behavior

of the products with barium carbonate it appears we are dealing with two groups; a neutral group, presumably aldoses, and a more acid group giving insoluble barium compounds, both characterized by the furfural reactions. The lines are obviously indicated upon which the separation and isolation of these two groups must proceed.

II. THE CONSTITUTION OF THE CEREALS STRAWS.

The straws are obviously complex structures and therefore not chemically homogeneous. They contain a considerable proportion of lignocellulose, the lignification being most marked in the groups of thickened polygonal cells situated in the hypodermal region, and evidently contributing chiefly to the rigidity of the stem.

The following constants[1] have been determined, certain of which may be taken as measuring the proportion of lignocellulose in the complex:

	Wheat straw.	Barley straw.
Cellulose, (chlorination method)	45.2	45.3
Chlorination, chlorine combining	2.5	2.5
" chlorine as hydrochloric acid	2.9	2.4
Methoxyl, ($O.CH_3$)	3.1	2.1
Furfural	14.15	14.15
Volatile acid, chiefly acetic, distilled with thirty-three per cent. sulphuric acid	6.4	6.3

The chlorination numbers correspond with a proportion of lignocelluloses amounting to thirty-three per cent. Of the cellulose isolated by the method of chlorination approximately one-half is obtained from this group, one-half being derived from the residual complex. The lignocelluloses, giving seven to eight per cent. furfural, yield say two and six-tenth of the total fourteen and five-tenths of the straw.

The "residual" complex is therefore richer in furfuroids and has a correspondingly lower proportion of the resistant celluloses.

It may be further resolved as follows:

		Yielding furfural of cellulose, per cent.	of straw, per cent.
Resistant "cellulose"	25.0	12.0	3.0
Pentosans, Hemicelluloses	42.0		9.0

[1] *Vide* the author's book: "Cellulose," pp. 111-113.

Assuming that of the latter group of easily hydrolyzable constituents the furfural-yielding bodies are exclusively pentosans, this would amount to one-half, and the entire straw (structural elements) might be expressed in terms of its proximate constituents, as follows :

Disposition in stem.			Containing cellulose.	Yielding furfural.
Hypodermal fibers and fibers of fibrovascular bundles.	Lignocelluloses ...	33.0	25.0	2.6
Vessels of fibrovascular bundles parenchyma and corbex.	Resistant cellulose.	25.0	2.50	2.6
	Hemicelluloses	21.0	...	..
	Pentosans	21.0	...	9.0
		100.00		14.6

It will be an object of our future investigations further to differentiate this complex.

4 NEW COURT, LONDON, W. C.

NOTES UPON THE DETERMINATION OF NITRITES IN POTABLE WATER.

BY AUGUSTUS H. GILL AND H. A. RICHARDSON.

Received October 29, 1895.

IN comparing the results obtained by Trommsdorff's iodo-zinc starch method and Griess' α-napthylamine test upon a large variety of waters, discrepancies were noticed which were very marked in the case of the peaty waters. These showed no blue by Trommsdorff's method, but in some cases as high as 0.0010 parts nitrogen as N_2O_3 per 100,000 by the Griess test. Upon decolorizing the waters the results agreed, showing that the peaty matter interferes with the formation of the iodide of starch, and unless nitrites are present in considerable quantity (above 0.0020 parts nitrogen as N_2O_3 per 100,000) this test is not capable of detecting them.

The decolorization was affected in the cold, as heating increases the nitrites, by shaking up about 250 cc. of the water with three cc. of "milk of alumina,"[1] allowing to settle, and filtering through a filter which is washed free from nitrites. Even when using Griess' method it was found advantageous to decolorize the peaty waters, as their brown color modifies the pink tint, giving a slightly higher reading than would otherwise be obtained.

[1] Prepared by precipitating a boiling solution of 125 grams potash alum per liter with ammonia, allowing the aluminum hydroxide to settle and washing by decantation.

COMPARISON OF METHODS FOR QUANTITATIVE ESTIMATION OF NITRITES.

Parts Nitrogen as N_2O_3 in 100,000.

		0.0000	0.0001	0.0005	0.0010	0.0015	0.0020
Decolorized tap water.	Naphtylamine	Mere trace of color.	The gradation was excellent and the color fully developed in twenty minutes, the highest standard developed immediately.				
	Iodo-zinc starch	Not a trace of blue.	The color did not fully develop until the expiration of five hours, although there was a faint color in the higher standards in an hour.				
	m-Phenyl diamine	Not a trace of color in any of the standards.					
Tap water (Cochituate).	Naphtylamine	Some color, *i. e.*, in nitrites in Cochituate.	Excellent gradation, color developed in twenty minutes, but the color was modified by the coloring matter in the water, thus being difficult to read.				
	Iodo-zinc starch	Did not develop.	Did not develop.	Did not develop.	Developed in eighteen hours.	Developed in eighteen hours.	Developed in eighteen hours.
	m-Phenyl diamine	No increase in color over that originally in Cochituate water.					
Water free from ammonia.	Naphtylamine	The gradation was excellent and the color fully developed in twenty minutes. The reading of the Cochituate to which no nitrites had been added was 0.0004.					
	Iodo-zinc starch	The color did not fully develop until the expiration of five hours, but at the end of that time there was color in all the tubes, even the very lowest.					
	m-Phenyl diamine	Not a trace of color in any of these standards.					

The table on the preceding page shows the effect of the peaty matter and also a comparison of the methods, together with that of the *m*-phenylene diamine.

In some cases a pink color was obtained and no blue, due probably to the greater delicacy of the napthylamine test, it being competent to detect 0.0001 part of nitoogen as N_2O_3 in 100,000. This we think is the extreme limit of the test, as different *shades*, not *depths* of color are obtained upon adding different quantities of the reagents, as Dr. J. T. Tanner[1] found. The iodo-zinc starch method is incapable of detecting less than 0.0002 part of nitrogen as N_2O_3 per 100,000.

In a few cases a blue color appeared, but no pink, but upon passing carbon dioxide through the water no blue was obtained. This may possible have been due to hydrogen perioxide. Where large quantities of nitrites are present, a purple color instead of a blue is obtained, which is difficult to estimate ; in such cases the water should be diluted before applying the test.

In conducting the Griess test, the directions given by Dr. Tanner[2] were followed with the additional precaustion of using water free from nitrites in the preparation of the reagents. This was prepared by distilling the middle portion of ordinary distilled water with an excess of alkaline permanganate, collecting the middle portion of the distillate thus obtained. Water prepared in this way gives no test upon eighteen hours' standing, even when tightly stoppered.

A GRAVIMETRIC METHOD OF ESTIMATING PHOSPHORIC ACID AS AMMONIUM PHOSPHOMOLYBDATE.[3]

BY THOMAS S. GLADDING.

Received November 11, 1895.

THE estimation of phosphoric acid by weighing the yellow precipitate of ammonium phosphomolybdate has often been attempted, but, except in iron analysis, where the amount of phosphorus is very small, such a method has never yet been successful. The reason of such failure is evident when we consider the analyses that have been made of the yellow precipitate. A few only need be presented.

1 Report National Board of Health, *1882*, 280.

2 *Loc. cit.*

3 Read before the New York Section of the American Chemical Society, Nov. 8, 1895.

	Rammelsberg.	Struve and Svanberg.	Sonnenschein.	Gibbs.
H_2O	5.77	9.49	11.23	3.94
NH_4OH	3.25	9.49	11.23	3.35
P_2O_5	3.90	3.63	3.03	3.66
MoO_3	86.45	86.88	86.87	89.05

Gibbs gives the following formula for the salt:

$$24MoO_3, P_2O_5, 3(NH_4)_2O+24MoO_3, P_2O_5 2(NH_4)_2O.H_2O+16Aq.$$

He prepared the salt by mixing solutions of ammonium molybdate (seven parts of water to three of the salt) and phosphate, adding nitric acid in excess to the solution and boiling. Such a method would give more or less occluded molybdic oxide. His analysis gave 3.70 per cent. and 3.83 per cent. of phosphorus pentoxide against the theoretical percentage of 3.66. Such results were sufficiently accurate for his purposes, but would discourage any suggestion of using the yellow salt as the basis of a gravimetric method. His formula is, however, without any doubt, the correct one, with the exception of the water of crystallization.

My own analysis of the salt precipitated in the manner described later on, and dried at a temperature of 105° C. to a constant weight, gives me the following composition:

	Theoretical.	By analysis.
$48MoO_3$	91.38	91.36
$4P_2O_5$	3.76	3.76
$10NH_3$	2.25	2.31
$11H_2O$	2.61	2.57

For ammonia 1.016 grams gave 0.234 gram NH_3 = 2.30 per cent.

For ammonia 20.193 grams gave 0.4690 gram NH_3 = 2.32 per cent.

For moisture 7.25 grams gave ——— = 2.53 per cent.
" " 10.30 " " " = 2.61 " "

The water was determined by estimating total hydrogen by combustion with copper oxide.

For phosphoric acid, repeated analyses and syntheses gave almost exactly 3.76 per cent.

The molybdic acid was found by difference.

The fact that drying at 105° C. expels all the water except

eleven molecules, and that the yellow salt when dried over sulphuric acid in a closed desiccator comes to the same weight as when dried at 105° C, would indicate that this salt contains no other water of crystallization. Any excess of water is apparently hygroscopic water and not water of crystallization. I therefore find the following as the correct formula for the crystallized yellow salt:

$24MoO_3, P_2O_5, 3(NH_4)_2O + 24MoO_3, P_2O_5, 2(NH_4)_2O, H_2O + 5Aq.$

The following method of procedure has given me a precipitate of a very uniform composition and would seem to afford the simplest and easiest method yet presented for estimating phosphoric acid.

To the solution of phosphoric acid, (twenty-five cc. to fifty cc. in bulk, are adden) twenty-five cc. of strong ammonia 0.900 sp. gr.: nitric acid, 1.42 sp. gr., is now added to acidity. The beaker containing the solution, is placed in a water-bath maintained at a constant temperature of 50° C. The ordinary ten per cent. acid molybdate solution is now added from a burette at the rate of about three drops per second, with constant stirring (fifty cc. may be added in five minutes). When the molybdate solution to an excess of about ten cc. has been added, the beaker is allowed to remain for ten minutes in the bath. The contents are then filtered through a weighed filter paper.

The filtrate, without the washings, and after the addition of five cc. molybdate solution, is replaced in the bath for ten minutes. The liquid should remain clear or at most show only a faint opalescence.

For washing the precipitate, a wash water of dilute nitric acid 100 : 1 is employed. Three generous washings by decantation and three washings on the paper followed by one final washing with distilled water are sufficient. The paper and contents are now drained for a few minutes on some waste filter or blotting paper and then dried to a constant weight at a temperature of 105° C.

In this method, the formation of a pure granular precipitate of uniform composition and free from occluded salts, is secured by the gradual addition drop by drop of the molybdate solution

with constant stirring. The completeness of precipitation of the phosphoric acid is attained by the presence of a large amount of ammonium nitrate. The separation of the molybdic oxide or iron salt is avoided by the low temperature employed.

For the final drying at 105° C. an air-bath was tried and decisively abandoned. The use of a liquid boiling at 108° C. to 110° C. is the only safe course. A water-oven consisting of several distinct divisions or floors, one above the other, and surrounded with dilute glycerol 1.160 sp. gr. boiling at 110° C. was found to work admirably. The lower bath or division is reserved for the final drying. None but dry or almost dry precipitates must be allowed in this lower division. The precipitates may be dried in an ordinary water-oven almost to a constant weight and then dried for one hour longer in a glycerol oven at 105° C. The filter papers used are dried at 105° C, and weighed between large, closely fitting ground watch-glasses. The final weighings of papers and contents are made in the same manner.

The following investigation serves to show the results that are secured by this method of analysis.

A chemically pure microcosmic salt was finely pulverized. Careful ignition of ten grams in a covered platinum dish gave 4.8955 grams of sodium phosphate, giving a percentage by calculation of 34.07 per cent. phosphorus pentoxide. Ten grams of the salt were now dissolved in one liter of water and aliquots taken. Twenty-five cc. containing 0.250 gram of microcosmic salt were treated exactly as above. Fifty cc. containing 0.500 gram microcosmic salt were treated by the official magnesia method. The following results were obtained:

	Taken.	Gladding method. Per cent.	Taken.	Magnesia method. Per cent.
1	0.250	34.07	0.500	34.07
2	0.250	34.08	0.500	34.05
3	0.250	34.06	0.500	34.09
4	0.250	34.10	0.500	34.08

A solution of one-tenth of the above strength was obtained by dilution. Of this the following quantities were used and the phosphoric acid therein obtained by the new method:

	Taken. cc	Yellow salt obtained.	Phosphorus pentoxide obtained.	Theoretical phosphorus pentoxide.
1	10	0.091	0.00342	0.003407
2	1	0.010	0.00037	0.00034

These last experiments demonstrate the insolubility of the yellow salt and the applicability of the new method to very small amounts of phosphoric acid.

A number of comparative tests of fertilizers gave closely agreeing results, as follows:

	Official method. per cent.	New method. per cent.
Phosphoric acid	28.80	28.87
" "	2.63	2.70
" "	12.03	12.00
" "	28.30	28.33
" "	15.64	15.70
" "	15.04	15.00
" "	15.19	15.23
" "	29.16	29.23

In all fertilizer work 0.250 gram were used for precipitation, and molybdate solution to an excess of about ten cc. was added. No more than ten cc. in excess should be used.

Tankages and fertilizers containing a notable amount of organic matter should be ignited before solution.

An application of this method to the direct determination of reverted or citrate soluble phosphoric acid promises good results. The method of procedure is as follows: The citrate filtrate and washings are made up to 200 cc. Twenty-five cc., equivalent to 0.250 gram of the fertilizer, are treated as follows: Fifty cc. ammonia 0.900 sp. gr., are added and then nitric acid to acidity. The liquid is now diluted to half a liter to overcome the solvent action of the ammonium citrate, and heated in a bath to 65° C. Fifty cc. of molybdate solution are added in a thin stream with stirring and the whole digested for thirty minutes. The rest of the analysis is conducted precisely as in ordinary work, except that the filtrate is heated for thirty minutes longer at 65° C. The liquid should remain clear.

DIPYRIDINE TRIMETHYLENE DIBROMIDE, AND A STUDY OF CERTAIN ADDITIVE REACTIONS OF ORGANIC BASES.[1]

By R. F. Flintermann and A. B. Prescott.

Received November 4, 1895.

IN the course of an inquiry into certain limits to the formation of the addition compounds of amines with halogen substituted hydrocarbons, an inquiry made both historically and by experimentation, the compound named first above was obtained. In this study the bases chiefly considered are the tertiary amines, and the halogen compounds chiefly those of mono- and dihalogen substitution, especially in the saturated hydrocarbons.

ALKYL HALIDES IN THE FORMATION OF NITROGEN BASES.

Among the more simple aliphatic bases, it is obvious that there are limits (other than those of valence) to the concentration of carbon, or displacement of hydrogen, in the atomic positions next but one to the nitrogen.[2] Among well known products, notmal propyl forms a primary, a secondary, and a tertiary amine, likewise a quaternary[3] base iodide, and hydroxide, the latter not decomposed at 100° C. In contrast, isopropyl has been found to form only a primary and a secondary amine. The butyls, as base-forming alkyls, behave with a like gradation of formative power. Normal butyl holds the four ammonium valencies of nitrogen.[4] Isobutyl, primary, forms the quaternary base iodide,[5] but not bromide.[6] Secondary butyl forms the secondary amine but sparingly, the tertiary with difficulty, and this refuses to unite with iodide of the same alkyl in formation of a quaternary base.[7] Finally the teritary butyl appears to form only a primary amine, namely, trimethyl carbinamine, $(CH_3)_3CNH_2$.[7]

This was obtained by Butlerow,[8] as a bye-product, from tertiary butyl cyanide, during the conversion of this nitrile to tri-

[1] Read at the Springfield Meeting of the American Association for the Advancement of Science.

[2] That is, as atoms directly linked to *alpha* C.

[3] H. Roemer, 1873: *Ber. d. chem. Ges.*, 6, 1101.

[4] Lieben and Rossi, 1873: *Ann. Chem.* (Liebig), 165, 109.

[5] Sachtleben, 1878: *Ber. d. chem. Ges.*, 11, 733.

[6] Reimer, 1870: *Ber. d. chem. Ges.*, 3, 756.

[7] S. Reimann, 1874: *Ber. d. chem. Ges.*, 7, 1289.

[8] *Ann. Chem.* (Liebig), 170, 151: 162, 7, 12.

methyl acetic acid, and has been obtained, as stated, through transformation of isobutyl iodide, when acted upon by silver cyanide, by Linnemann,[1] and by Brauner.[2] Rudneff,[3] also has studied trimethyl carbinamine. The last named chemist found that although trimethyl carbinamine unites with tertiary butyl iodide to form the secondary base in its hydriodide, $(CH_3)_6C_2NH.HI$; on distilling this with potash the secondary amine was not formed, but only the primary amine again. This boils at 45° C. The preparation of trimethyl carbinamine by transformation of isobutyl iodide in reaction with silver cyanate, as reported by Linnemann,[4] was tried by A. W. Hofmann, in 1874,[5] without success, obtaining chiefly isobutylamine, after which Brauner, at Linnemann's request, went over the work with great care, and has reported the operation with his interpretation of the reaction and his successful production of the primary amine of the tertiary alkyl, as above cited. He obtained, however, both isobutylamine and the tertiary butylamine. In repeating his operation twice, the second time with rigid rectification of materials and products, we obtained the hydrochloride of a base which agrees in centesimals with a pure butylamine. On distilling this over potassium hydroxide, no distillate was obtained of a boiling-point below 65° C. The first distillate had just the boiling-point of isobutylamine, primary amine of primary alcohol, a result which only gives to us another indication that tertiary alkyls do not form amines with readiness.

The greater avidity of methyl halides than of ethyl halides, in additive reaction with tertiary bases, is a common laboratory observation. This difference, however, cannot be attributed wholly to the ratio of hydrogen carried by the carbon atom linking to nitrogen, because of the higher ratio of total hydrogen to total carbon in the methyl as compared with entire ethyl. But the disparity in reactive strength between propyl and isopropyl can be theoretically attributed to the one difference between the two alkyls, the structural difference in ratio of hydrogen to car-

1 1872: *Ann. Chem.* (Liebig), 162, 19.

2 1878: *Ann. Chem.* (Liebig), 192, 65.

3 1878: *Ber. d. chem. Ges.*, 11, 988, 1938: 12, 1023: 1880. Bull. Soc. chim. [2], 33, 297.

4 Already cited. This transformation agrees with that of isobutyl alcohol into trimethyl carbinol, reported at the same time by Linnemann: *Ann. Chem.* (Liebig), 162, 12.

5 *Ber. d. chem. Ges.*, 7, 508.

bon in positions nearest the nitrogen. In speed of additive reaction toward trimethylamine, Menschutkin[1] found that of normal propyl iodide to be 0.0116, that of isopropyl iodide to be 0.00121, in like measures of the two. Normal butyl was to isobutyl as 0.00832 to 0.00191. Ethyl to normal propyl as 0.00584 to 0.000984, all the alkyls acting as iodides, the reactions being compared in the same solvent. In recent studies[2] of the same investigator, tertiary amines are compared with secondary and primary amines in speed of additive reaction with the same alkyl bromide, in each of four series. Toward methyl bromide, diethylamine is to dipropylamine, as 16886 to 10264; toward ethyl bromide, the same amines, respectively, as 182 to 101, in speed of addition. Using electrolytic measurement of the affinity coefficients, Bredig[3] finds the quaternary organic bases to be the strongest and the tertiary the weakest, each taken in its ammonium chloride.

The limits of the addition of aliphatic tertiary base, those of simple composition, to halogen substituted hydrocarbons, have been lately studied by Kleine,[4] the chief question being the additive capacity of a secondary, and a tertiary, halogen substituted group. The bases studied were trimethylamine and triethylamine: the halides were monobromine and dibromine substituted hydrocarbons in the saturated series as far as pentane, as well as various unsaturated derivatives of open carbon chain. It was concluded by Kleine, from work previously reported and from some work of his own, that addition is not effected with the linking group CHX (X being the halogen), nor with a tertiary group CX, nor if a secondary or tertiary substituted group be present in the compound. Addition is not obtained with ethylidine bromide, nor with common propylene bromide, $CH_3.CHBr.CH_2Br$, nor with monobromethylene, nor with either *alpha* or *beta* monobrompropylene, nor with $CHBr:C(CH_3)_2$. In failure of addition other reactions take place, the products of which have been determined. Evidently the affinities of these

1 N. Menschutkin and M. Vasileff, St. Petersburg, April, 1890: *Ztschr. phys. Chem.*, 5, 589.

2 Menschutkin, 1895: *Ber. d. chem. Ges.*, 28, 1398.

3 G. Bredig, 1894: *Ztschr. phys. Chem.*, 13, 288.

4 G. Kleine, 1894: Chem. Centrbl., I, 16, from Ztschr. Naturwissenchaftens, 66, 1–72.

other products are factors in the problem as to the limit of alkyl union with nitrogen in organic bases.

In the studies of these limits phenyl has received less attention.[1] Diphenylamine is a weak base. Triphenylamine is indifferent to acids, and refuses addition with alkyl iodides. Triphenyl phosphine is stated to have a little capacity to hold alkyl iodides in union. Coming under the definition of a tertiary alkyl, phenyl has base-forming capacity distinctly greater than that of tertiary butyl, the interactions of all the CH groups in the ring in some way reinforcing the carbon which links to nitrogen, destitute as this carbon is in respect to direct hydrogen union. In pyridine there appears an altogether different character, an indivisible tertiary base of strength, with special additive capabilities. With alkyl iodides it forms certain addition compounds beyond those obtained even with trimethylamine. In pyridine the carbon linked to nitrogen is wholly in CH groups, and we may infer that all of the five of these groups are in some sense directly united to the nitrogen, though brought within a valence of three. Possibly also, the unsaturation of the unions of carbon to carbon, which is more active in pyridine than in benzene, imparts additive power to the nitrogen. The vigorous formation of pyridine methyl iodide was remarked by Anderson[2] shortly after his discovery of this base.

Mention of the addition compounds of pyridine with methyl iodide,[3] ethyl iodide,[4] propyl iodide and isopropyl iodide,[5] has been published in the accounts of various investigations devoted to other subjects, and therefore with partial examination and description of these particular products.[6] In resorting to pyridine as an analytical reagent for the identification of alkyls, Lip-

[1] In setting out to build up secondary and tertiary amines in 1850, A. W. Hofmann formed ethylphenylamine, remarking that his "previous experimental researches suggested aniline for the foundation."—Phil. Trans., 1850, I., 97.

[2] Trans. Roy. Soc. Edinb., 21, (4) 571; *Ann. Chem.* (Liebig), 94, 360.

[3] O. Lange, On picolines by Ladenberg's transposition, 1885: *Ber. d. chem. Ges.*, 18, 3436.

[4] O. de Coninck, Analytical distinction between pyridine and quinoline, 1883: *Bull. Soc. chim.* [2], 40, 276.

[5] Ladenburg and Schraeder, On formation of propyl pyridines, 1884: *Ber. d. chem. Ges.*, 17, 1:21, and further in other papers.

[6] A description of these four quarternary base iodides is given in another paper from this laboratory by A. B. Prescott.

pert[1] has recently reviewed the literature upon pyridine alkyl iodides, and has also contributed an account of the preparation, and certain of the properties of the obtainable butyl iodides of pyridine, namely, those of normal butyl, isobutyl, and secondary butyl. Tertiary butyl iodide did not form a permanent addition product with pyridine, in Lippert's hands, the reaction for its production yielding indications of pyridine hydriodide and of isobutylene. These transformation products are the same that have been obtained upon attempting to introduce tertiary butyl into aliphatic amines, and at all events have prevented the linking of more than one tertiary butyl group to the nitrogen of these amines.

It appears, therefore, that for secondary and tertiary alkyl halidies, the limits of pyridine addition go beyond the limits of trimethylamine or triethylamine addition, while the former limits are parallel to the latter. On the other hand it is easier to form a primary amine or ammoninm salt of a tertiary alkyl than it is to form a pyridinium salt of the same alkyl. Comparing pyridine addition with aliphatic base formation, we may apply the conclusions drawn by Menschutkin from comparisons among certain aliphatic bases themselves, that the capacity of the nitrogen atom in a base to exercise five units of valence, depends largely, he says, on the nature of the elements or groups to which the nitrogen is already united.

DIHALOGEN SUBSTITUTED HYDROCARBONS IN ADDITIVE REACTION WITH PYRIDINE.

The action of halidies of "diatomic radicals" upon the tertiary amines was studied by Hofmann in London.[2] Pyridine ethylene bromide was obtained[3] in his laboratory a short time before he returned to Germany. This product was stable, and upon analysis was found to have the proportions of $(C_5H_5N)_2$ $C_2H_4Br_2$. We may now express this composition by the formula

$$C_5H_5N{<}{}^{CH_2.}_{Br}{}^{CH_2}_{Br}{>}NC_5H_5.$$

[1] W. Lippert, On the decomposition of ethers by hydrogen halides, 1893: *Ann. Chem.* (Liebig), 276, 181.

[2] Phil. Trans. Action of ethylene bromide upon trimethylamine, May 2, 1858, upon triethyl phosphine, Jnne 25, 1860. Further Proc. Roy Soc., 9, 293.

[3] Davidson, May 24, 1861: Proc. Roy. Soc., 11, 261; *J. Chem. Soc.*, 14, 161.

The next homologue in diprimary dibromine substitution is trimethylene bromide, $CH_2Br.CH_2.CH_2Br$, and we have obtained its addition compound with pyridine as follows: Pyridine of a boiling-point of 116°–118° C., and trimethylene bromide of a boiling-point of 165° C., were added together in the proportion of two molecules of the pyridine to one molecule of the bromide, and to the mixture one-fifth its volume of absolute alcohol was added. In Preparation I the mixture was heated in a sealed tube, at 105°–115° C. for four hours, when the product was a light brown crystalline mass, with a very little dark brown oily liquid and some gas escaping as the tube was opened. The crystals were drained, washed with alcohol, becoming of very light color, and recrystallized once from alcohol, becoming nearly white. Dried on a porous plate, the melting point of the crystals was 225°–226° C. In Preparation II the same materials, in same proportion, were digested in a sealed tube without applying heat, for a week. Crystallization began in clusters on the first day and increased steadily until apparently complete, this product being pure white. These crystals, without recrystallizing, were washed under suction with alcohol and dried on a porous plate in a vacuum desiccator. The melting point was the same as that of Preparation I.

This compound is very soluble in water, less soluble in alcohol, and in ether, and but very slightly soluble in chloroform. It is slightly hygroscopic in the air. Kept in an open vessel for weeks it shows no indication of decomposition. At the high melting point there is gradual decomposition. Distilled at a little above its melting point, it yielded hydrobromic acid, and a very hygroscopic sublimate, which sublimed again unchanged, and had the properties of pyridine hydrobromide. No further work was done upon the decomposition products. Analysis of the addition product itself gave figures as follows:

	Calculated for $(C_5H_5N)_2C_3H_6Br_2$.	Preparation I. (1)	(2)	Preparation II.
Bromine	44.43	44.11	44.07	44.42
Nitrogen	7.78	8.08	8.46	7.84

A determination of the molecular weight was made with Preparation I by the cryoscopic method, using phenol as the solvent. Previous trial was made with acetic acid, the results of

which indicated decomposition of the addition product. Had time permitted making the determination with the purer product in Preparation II, obtained later, results closer to the calculated molecular weight than could have been expected. The figures obtained with Preparation I were as follows, in which $M =$ molecular weight; $K =$ constant, which for phenol is 76; $g =$ grams of substance; $G =$ grams of solvent, and $\Delta =$ depression. These are taken in the formula $M = 100.K.\frac{g}{\Delta G}$.

No.	g.	G.	Δ	M.
1	0.4055	15.5	0.573°	346.8
2	0.6898	15.5	1.083°	312.0
3	0.2339	16.6	0.328°	328.0
4	0.3386	15.7	0.492°	332.8
5	0.3852	24.8	0.340°	347.1
6	0.6914	24.8	0.651°	326.0
$(C_5H_5N)_2C_3H_6Br_2$				359.15

The formula, therefore, appears to be

$$C_5H_5N{<}^{CH_2.CH_2.CH_2}_{Br\qquad\qquad\quad Br}{>}NC_5H_5.$$

This determination supports the formula adopted for the pyridine ethylenebromide of Davidson, as a dipyridine compound. Hofmann[1] found the trimethylamine ethylenebromide to have the proportions of a monammonium compound, $(CH_3)_3N.C_2H_4Br_2$, while singularly enough, Kleine gives[2] the proportion in trimethylamine trimethylenebromide to be those of a diammonium compound $\left((CH_3)_3N\right)_2.C_3H_6Br_2$.

The composition of these four related dihalogen addition products, the aliphatic base and the aromatic base combinations respectively with substituted ethane and propane, may be compared as follows:

With trimethylamine:

The ethane derivative, $(CH_3)_3N{<}^{CH_2.CH_2Br.}_{Br}$

The propane derivative, $(CH_3)_3N{<}^{CH_2.CH_2.CH_2}_{Br\qquad\qquad\quad Br}{>}N(CH_3)_3.$

With pyridine:

The ethane derivative, $C_5H_5N{<}^{CH_2.CH_2}_{Br\qquad Br}{>}NC_5H_5.$

[1] 1858: Proc. Roy. Soc., 9, 293. "Addition of nitrate of silver precipitates only one-half of the bromine as bromide of silver, while even by protracted ebullition the second half remained untouched."

[2] Chem. Centrbl., 1894, I., 16.

The propane derivative, $C_5H_5N{<}{}^{CH_2}_{Br}.CH_2.{}^{CH_2}_{Br}{>}NC_5H_5$

As these results now stand, it appears, *first*, that pyridine is more reactive for addition with diprimary halogen groups than is trimethylamine ; *second*, that with the weaker base the one primary halogen group protects the other from addition when both these groups link together, not when they are separated by a CH_2 group. In this relation it may be noted as a conclusion of Bredig,[1] that in metameric diamines, the bases are stronger, the further removed are the amido groups.

We have studied the reaction of pyridine upon a few primary-secondary dihalogen substituted hydrocarbons, and have not obtained addition in any of these cases. The conditions of addition were digestion in sealed tubes at 80° to 100° C. Propylene bromide, $CH_3.CHBr.CH_2Br$, was treated in several operations, both with di-pyridine proportions and with mono-pyridine proportions, with the result of various products, but without an addition product. Pyridine hydrobromide was at all events obtained. Again, with ethylidine chloride no addition was obtained. Other conditions, however, will be brought to bear upon this class of pyridine additions, in work now in hand in this laboratory.

ANN ARBOR, MICHIGAN.

A PROPOSED SCHEDULE OF ALLOWABLE DIFFERENCE AND OF PROBABLE LIMITS OF ACCURACY IN QUANTITATIVE ANALYSES OF METALLURGICAL MATERIALS.[2]

BY E. D. CAMPBELL.

Received October 1, 1895.

WITHIN the past twenty years, metallurgical practice has grown to depend more and more upon a chemical knowledge of the material employed in the various operations. On account of this dependence it has become necessary to have accurate as well as rapid methods for the determinations of the elements which take an active part in the different processes.

Many methods for the determination of the various elements

[1] *Loc. cit.*

[2] Read before the Chemical Section of the American Association for the Advancement of Science, Sept. 2, 1895.

usually met with in metallurgical work have been proposed, each having its own claim for accuracy, or rapidity, or both, but as will be seen from the efforts of the International Committee on the analysis of Iron and Steel, we are far from having perfect methods for metallurgical analysis.

There are many sources of error in ordinary quantitative determinations, which, while they can be partly avoided, can never be wholly overcome. Among these may be mentioned such errors as arise from solubility of precipitates, solubility of apparatus in which operations are performed, impurities in chemicals, inaccurate graduation of volumetric apparatus, unavoidable error in accuracy of weighing, and last, but not least, errors due to what may be termed the personal equation, the presence or absence in the operator of that manipulative skill which distinguishes an expert from a clumsy worker. Since we cannot expect absolute agreement in results it may be asked how close should quantitative determinations agree. This question cannot be answered by a single figure since the unavoidable errors in the various determinations differ according to the element determined and the method used in the analysis. Just how great a difference between determinations should be allowed and what the probable limit of accuracy, which may be hoped for, is largely a matter of judgment based upon the examination of the results obtained by different chemists, known to be careful operators, working upon the same material.

Basing our judgment upon the usual errors of analysis, upon the commercial requirements of accuracy and upon the unavoidable sources of error we would propose the following schedule of allowable differences and of probable limits of accuracy for discussion in the section. In the table below the first column shows the element or constituent determined; the second, a formula for calculating the difference which might be reasonably expected between the results of two chemists working upon the same material and the third column shows a formula for calculating the probable minimum error which may be hoped for. To take an instance: suppose chemist A reports the phosphorus in a specimen of steels as 0.076 per cent., then by the formula in the table we might expect B to report 0.076 ± 0.00352 per cent.,

and from the third column we could not hope to reduce the error to less than 0.00058 per cent.

Element or constituent.	Allowable difference of per cent.	Probable limit of accuracy.
Iron and Steel.		
Graphitic carbon	$\pm[0.050+(0.02\times Cg)]$	$\pm[0.005+(0.005\times Cg)]$
Cast iron Combined carbon	$\pm[0.050+(0.92\times Cc)]$	$\pm[0.005+(0.005\times Cc)]$
Carbon in steel	$\pm[0.010+(0.02\times C)]$	$\pm[0.002+(0.003\times C)]$
Silicon	$\pm[0.005+(0.02\times Si)]$	$\pm[0.002+(0.003\times Si)]$
Sulphur	$\pm[0.003+(0.03\times S)]$	$\pm[0.0005-(0.005\times S)]$
Phosphorus	$\pm[0.002+(0.02\times P)]$	$\pm[0.0002+(0.005\times P)]$
Manganese in cast iron and steel	$\pm[0.005+(0.04\times Mn)]$	$\pm[0.001+(0.005\times Mn)]$
Manganese in spiegels, ferro, etc.	$\pm[0.050+(0.004\times Mn)]$	$\pm[0.005+(0.001\times Mn)]$
Nickel	$\pm[0.050+(0.02\times Ni)]$	$\pm[0.005+(0.005\times Ni)]$
Ores.		
Silica	$\pm[0.050+(0.006\times SiO_2)]$	$\pm[0.005+(0.001\times SiO_2)]$
Alumina	$\pm[0.030+(0.003\times Al_2O_3)]$	$\pm[0.005+(0.001\times Al_2O_3)]$
Ferric oxide	$\pm[0.030+(0.003\times Fe_2O_3)]$	$\pm[0.005+(0.001\times Fe_2O_3)]$
Iron	$\pm[0.020+(0.003\times Fe)]$	$\pm[0.004+(0.001\times Fe)]$
Manganese	$\pm[0.050+(0.003\times Mn)]$	$\pm[0.005+(0.001\times Mn)]$
Calcium oxide	$\pm[0.050+(0.002\times CaO)]$	$\pm[0.010+(0.001\times CaO)]$
Magnesia	$\pm[0.050+(0.010\times MgO)]$	$\pm[0.005+(0.002\times MgO)]$
Phosphorus	$\pm[0.002+(0.02\times P)]$	$\pm[0.0002+(0.005\times P)]$
Phos. pentoxide	$\pm[0.005+(0.02\times P_2O_5)]$	$\pm[0.0005+(0.005\times P_2O_5)]$
Combined water	$\pm[0.050+0.10\times H_2O)]$	$\pm[0.010+(0.001\times H_2O)]$
Potassium oxide Sodium oxide	$\pm[0.050+(0.020\times K_2O)]$	$\pm[0.005+(0.005\times K_2O)]$
Sulphur in iron ore	$\pm[0.005+(0.030\times S)]$	$\pm[0.001+(0.003\times S)]$
Sulphur in pyrite	$\pm[0.050+(0.004\times S)]$	$\pm[0.005+(0.0002\times S)]$
Lead	$\pm[0.050+(0.003\times Pb)]$	$\pm[0.005+(0.0005\times Pb)]$
Zinc	$\pm[0.050+(0.003\times Zn)]$	$\pm[0.005+(0.0005\times Zn)]$
Copper	$\pm[0.030+(0.003\times Cu)]$	$\pm[0.005+(0.001\times Cu)]$
Nickel	$\pm[0.030+(0.003\times Ni)]$	$\pm[0.005+(0.001\times Ni)]$
Arsenic Antimony	$\pm[0.050+(0.010\times As)]$	$\pm[0.002+(0.001\times As)]$
Tin	$\pm[0.010+(0.010\times Sn)]$	$\pm[0.005+(0.001\times Sn)]$
Coal and Coke.		
Moisture	$+[0.050+(0.020\times H_2O)]$	$\pm[0.005+(0.005\times H_2O)]$
Vol. hydrocarbon	$\pm[0.050+(0.10\times hydro)]$	$\pm[0.010+(0.001\times hydro)$
Fixed carbon	$\pm[0.050+(0.010\times C)]$	$\pm[0.010+(0.001\times C)]$
Sulphur	$\pm[0.020+(0.030\times S)]$	$\pm[0.005+(0.003\times S)]$
Ash	$\pm[0.050+(0.005\times Ash)]$	$\pm[0.005+(0.001\times Ash)]$
Phosphorus	$\pm[0.002+(0.02\times P)]$	$\pm[0.0002+(0.005\times P)]$

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 10.]

DERIVATIVES OF COLUMBIUM AND TANTALUM.[1]

BY MARY ENGLE PENNINGTON.

Received November 29, 1895.

AMONG the more metallic members of Group V of the Periodic System are the elements columbium and tantalum, which, though almost a century old and counting among their devotees such investigators as Rose, Hermann, Marignac, Rammelsberg, and others of equal fame, still offer many interesting problems to the student of inorganic chemistry. Comparatively few of the compounds of these elements have been prepared. Those which have been studied narrowly enough to afford an accurate knowledge of their chemical behavior form a much shorter list. The early literature is, in many instances, very contradictory, due to the supposed existence of such elements as pelopium and ilmenium, engendering as they did the fruitful controversy between Hermann and Marignac, which controversy resulted in the tacit acceptance by the chemical world of Marignac's statement, that columbium is elementary. The old doubt, however, appears to have been revived through the very careful work of Krüss in 1887, on the oxides of these metals, their separation from each other and also from the oxides which accompany them in their apparent minerals.

He found through the fractional crystallization of the double fluoride of columbium and potassium, and by determining the atomic value of the various fractions, that something apparently contaminated the columbium. In some fractions the values obtained were far too low. This he accounted for by proving the presence of titanium. Other portions, however, were much too high, and this, it was carefully proved, was not due to adhering tantalum. Just what the substance was which gave in one fraction an R^v having almost double the accepted atomic mass was left undecided.

A careful consideration of this question in the light of the various researches, makes it seem not improbable that the compounds of columbium, as we know them, are not perfectly free

1 From the author's thesis presented to the University of Pennsylvania for the degree of Ph. D., 1895.

from contaminating substances. The many difficulties encountered in the separation of this oxide from others usually occurring with it, and the insufficiency of the prevailing methods of separation, seem to demand a more exact knowledge of the behavior of the element in the purest condition obtainable, and also when mixed with the oxides of tantalum and titanium which usually adhere to it.

It was with the hope that some additional light might be thrown upon the general deportment of the derivatives of these elements that this research was undertaken.

The material used was obtained from a columbite from Wakefield, N. H. An abundant supply of the mineral was secured through the kindness of Professor S. P. Sharples, of Boston, in whose possession it had been for some years though it had never been analyzed. Wakefield is a new locality for columbite. The deposit was discovered while mining for feldspar. Near the columbite is quite a deposit of beryl.

ANALYSIS OF WAKEFIELD COLUMBITE.

The mineral occurs in large, black, lusterless masses. Scattered over the surface are little patches of a bright yellow substance. These proved to be uran-ochre and gave evidence of the presence of the uranium which was later found in the mineral. Feldspar occassionally penetrated the mass, though in small quantity. The specific gravity of picked material was found to be 5.662 at 4° C.

Decomposition was effected by the method usually employed for this class of minerals.

Fusion with Acid Potassium Sulphate.—The finely divided mineral was allowed to stand over calcium chloride for some hours. The desired amount of this dry, and almost impalpable, powder was weighed off and mixed with at least nine times its weight of fused potassium bisulphate. This must be an intimate mixture. Great care should be exercised when the heat is first applied, else loss by spattering will occur. Frequent stirring tends to prevent this, and also hastens the decomposition.

Some trouble was experienced by the fusion "climbing" and

leaving far up on the sides of the crucible particles of mineral which could neither be driven down by heat or forced down by a platinum rod. To collect these particles the crucible containing the clear, quiet fusion was slightly tilted and the adhering portions covered with a little bisulphate. Then by gently heating the whole mass was driven down until it met the main portion of the fusion. All decompositions by this method were made in a large platinum crucible or platinum dish. The latter was preferred. If the mineral is fine enough the fusion is complete in about five hours.

The fused mass was taken up in a large quantity of water, and boiled out with water several times. The insoluble portion consisted of the oxides of columbium, tantalum, titanium, tin, tungsten, and any silica which was present. Small quantities of these oxides invariably remained dissolved although the solution was boiled for a long time; it is, therefore, advisable to let the filtrate stand twenty-four hours, then refilter.

The moist oxides, according to Headden,[1] should "be digested with yellow ammonium sulphide" to remove all tin, tungsten, etc. Rose recommends that yellow ammonium sulphide should be simply poured over them, and that this solution should be evaporated to dryness, and gently ignited, to render the columbium and tantalum oxides which have been dissolved by the alkali, insoluble. Wöhler[2] claims that it is sufficient to treat the metallic oxides upon the filter with yellow ammonium sulphide. As some uncertainty existed as to the best course to pursue, the effect of ammonium sulphide when mixed with these oxides for a longer or shorter period of time was studied.

Heating in a porcelain dish on the water-bath for three hours gave 1.15 per cent. of the mixed oxides; one and one-half days, 1.60 per cent.; three days, 1.85 per cent.; one week, 2.24 per cent. By pouring the sulphide over the oxides on one filter, as Rose and Wöhler advise, 0.24 per cent. of the mixed oxides was obtained.

Apparently, the moist metallic oxides are more readily dissolved by ammonium sulphide than is generally supposed, and,

[1] *Am. J. Sci.*, 41, 91, *1891*.
[2] Mineral Analyze, p. 140.

therefore, when working with columbites containing the acid oxides care must be taken, or a very appreciable error may result.

The ammonium sulphide solution was precipitated by dilute hydrochloric acid, and the precipitate was filtered, and washed with hydrogen sulphide water, alcohol, ether, carbon disulphide and ether. The mixed sulphides were carefully heated in the air, then reduced in a current of hydrogen gas. The residue treated with dilute hydrochloric acid gave tin in solution and left undissolved a small quantity of a black compound which proved to be the tetroxide, Cb_2O_4, with possibly a little tantalum.

The moist oxides when treated with ammonium sulphide, have not only the acids removed, but the iron contained in them is changed to sulphide. This is dissolved out by dilute sulphuric acid. Filter off the oxides and wash them thoroughly with boiling water. A pump is usually necessary because of the precipitate being finely divided, and having a tendency to clog the pores of the filter. By this treatment the oxides should be entirely freed from iron and manganese. Nevertheless ignition gave a powder having a distinct pinkish yellow hue, showing the presence of these elements. The oxides were, therefore, re-fused with potassium bisulphate and treated as before. The second fusion gave a product lighter in color, yet not perfectly white. Another fusion was resorted to, and no loss in weight was observed, as a small amount of iron still adhered to the oxides. In fact, a *perfectly white* mixture of the oxides has not been obtained by this method.

The sulphuric acid solution of the iron which remained with the insoluble oxides, was added to the aqueous extraction of the fusion. This solution now contained iron, manganese, uranium, and calcium, with a large excess of sulphuric acid and alkali salt. Yttrium, cerium and calcium were looked for according to the plan presented in Rose's Handbuch der analytischen Chemie, **2**, 335, which is, in brief, this: The greater part of the free acid is neutralized with sodium carbonate; sodium acetate is added, so that acetic acid is in large excess. The earths are precipitated by ammonium oxalate, the precipi-

tate being allowed to stand twenty-four hours. From three grams of mineral only a very small amount was obtained. This was too small a quantity to investigate further, so that if any rare earths are present in the mineral they exist in traces.

To the filtrate which contained iron, manganese and uranium were added ammonium sulphide and ammonium carbonate. The iron and manganese were precipitated as sulphides, while uranium was held back by the ammonium carbonate. Beryllium, if present, would have been found here. This element was sought for, since the locality from which the mineral came made it a probable constituent, but none was detected. The sulphides having been filtered out, the filtrate was made acid with hydrochloric acid, the carbon dioxide boiled off, then the uranium precipitated by ammonium hydroxide. The uranium hydrate was filtered, washed, ignited, and weighed as U_3O_8. The sulphides of iron and manganese were dissolved off the filter in hydrochloric acid, oxidized, and separated by the basic acetate method, the manganese being finally weighed as manganese pyrophosphate.

The water contained in this columbite was determined by heating in a boat in a glass tube, and collecting the aqueous vapor in a weighed calcium chloride U tube.

In the literature relating to columbites and allied minerals, while a ferrous content is given, the method by which it was determined is omitted. Perhaps this is due to the fact that the customary decomposition with sulphuric acid in a sealed tube naturally suggests itself, yet in applying this course to the columbite under examination unexpected difficulties were encountered. The experience is at least interesting.

The mineral was ground very fine and heated in sealed tubes with sulphuric acid (one part of concentrated acid to two parts water), the resulting decomposition being titrated with permanganate with the following results :

	Per cent. FeO.
0.5 gram heated one day at 210° C	1.316
0.5 gram heated two days at 230° C	1.416
0.5 gram heated five days at 230° C	5.50

It seemed probable that this was not the total amount of fer-

rous iron in the columbite, hence attention was directed to an old method which is rarely used, yet seems to be worthy of greater attention than has been given it. Berzelius first suggested the method, though it is generally credited to Hermann. The finely ground mineral is mixed with fused and finely divided borax. A small platinum crucible is completely filled with this mixture, then covered with a platinum lid, and the whole placed in a larger platinum crucible. Dry magnesium oxide is packed around and over the inner crucible until it is completely covered and so excluded from air contact. The heat of a good Bunsen lamp is applied for one-half hour, when the decomposition is complete. Longer heating, or too rapid cooling, causes the fusion to adhere very tightly to the crucible, and loss may result on endeavoring to remove it. When the whole is quite cold, the small crucible is taken out, freed from adhering magnesium oxide, and weighed. The fusion, which is a clear green glass, is then freed from the crucible by sharply tapping; a piece may be broken off, weighed, ground in a mortar, dissolved in water and sulphuric acid, and titrated with potassium permanganate. Or, if the amount of ferrous iron is not large, it is better to crush the whole fusion in a diamond mortar, then place in a flask provided with a Bunsen valve, dissolve in water and sulphuric acid, and titrate. To prevent the oxidation of the iron during its solution, a quantity of sodium carbonate was placed in the flask with the ground fusion, and the water and sulphuric acid added carefully to this mixture. When a strong evolution of carbon dioxide had continued for several minutes, the cork carrying the Bunsen valve was quickly inserted, and the flask put aside until solution had taken place. It is necessary to shake the flask from time to time, otherwise the finely divided oxides which separate will enclose some particles of the fusion, and the result will be low. In one or two hours the insoluble residue should be a perfectly white, fine homogenous mass. The flask is then opened, more sulphuric acid added if necessary, and the iron titrated with permanganate. A number of fusions were made according to this method, the amount of ferrous oxide found being 6.426 per cent. The method seems to be, so far as columbite is concerned, perfectly trustworthy. It

is rapid, and the manipulation is not difficult. The oxides which separated out were perfectly white. In one experiment they were filtered off, washed with hot water, ignited, and weighed. The percentage of mixed oxides, 77.94 per cent., agress quite well with that obtained by the bisulphate method.

The quantitative analysis ot this columbite by fusing with bisulphate, as above described, gave the following results :

	A.	B.	C.	D.	E.
Ta_2O_5, Cb_2O_5, TiO_2	78.61	79.04	79.04	77.96	78.70
Fe_2O_3	12.30	13.83	13.62	13.58	....
SnO_2, WO_3	1.15	1.60	1.85	2.24	1.84
MnO	8.96	8.32	....	8.08	....
	101.02	102.79	....	100.86	....

One-half gram of material was used in each case. The ferric oxide, as given above, includes the ferrous, which, estimated by the method of Berzelius, equals 6.42 per cent.

In a sixth analysis three grams of material were taken, and due attention was paid to those constituents which former analyses had shown to be present, but in such small quantities that their determination was not trustworthy. The results in this case were :

	Per cent.
Ta_2O_5, Cb_2O_5, TiO_2	78.04
WO_3, SnO_2	0.24
U_3O_8	0.48
Fe_2O_3	5.22
FeO	6.42
CaO	0.02
MnO	8.96
H_2O	1.22
Total	100.60

An interesting point in the composition of this columbite is the ferric oxide. Hermann records one analysis of some fragments of a columbite from Miask containing several per cent. of it, and so far as I am aware this is the only columbite in which

this constituent is mentioned. He also gives a Miask columbite containing 0.50 per cent. of uranium oxide. Genth mentions a trace of uranium in a columbite analyzed by him.

While no effort was made to separate the metallic oxides quantitatively, it was found from the preparation of pure material that the columbium was in decided excess. Titanic acid was proved to be present, and silica was found in very small quantities.

Many of the recorded analyses in which separations of columbic and tantalic oxides are given, fail to state whether any attempt had been made to eliminate or to prove the presence of titanium or silica. Given a mixture of tantalum, columbium, and titanium, the analyst will have no difficulty in separating tantalum from columbium by Marignac's double fluoride method. But the titanium double fluoride, when mixed with the columbium salt, shows an abnormal solubility which makes its separation very doubtful. This point will be more fully discussed later.

Fusion with Sodium Thiosulphate.—It occurred to me to try the decomposition of the mineral by fusion with sodium thiosulphate, believing that in this way tungsten and tin would be converted into sulpho salts, and could then be more effectually removed from the other constituents. Without entering into detail, I may say the attempt was fruitless.

Decomposition of the Gibbs Method.—Some years ago Dr. Gibbs published a procedure[1] for the decomposition of the columbite minerals; and as my desire was to investigate the different methods of decomposition, I naturally turned to this suggestion. In mineral literature this course is given a second place to the bisulphate decomposition. My own experience compels me to prefer it to the latter method. The details of the Gibbs method are, in brief, as follows:

The mineral must be fine, yet need not be in an impalpable powder, as is necessary in the bisulphate decomposition. It was intimately mixed, by grinding in a mortar, with three times its weight of potassium fluoride; the mixture was transferred to a platinum crucible and made into a paste with concentrated

[1] *Am. J. Sci. Arts.*, 37, 357. 1864.

hydrofluoric acid. The mass heated up at once, and for some minutes the decomposition proceeded without the application of heat. It was found advantageous to let this mixture of acid salt and mineral stand for several hours, stirring occasionally, and adding more acid if the mass became hard. It was then heate l on a water-bath until the excess of acid was driven off. After thoroughly drying on an iron plate, the free flame was applied. Hydrofluoric acid was driven out of the acid potassium fluoride, and at length the whole mass fused and formed a clear, quiet, easily handled fusion, which upon cooling, became a beautiful pink-violet in color.

The decomposition is not complete until every part of the mixture has assumed this color, which does not change on further heating. In the early part of the fusion a deep blue color appears.. If the action be interrupted at this point, an incomplete decomposition will result.

The violet mass was taken up with water and hydrofluoric acid in a platinum dish, then boiled and filtered. This extraction should be repeated several times. If the decomposition is not quantitative, the solution in water is much hastened by first grinding the fusion. Any silica which may have been present in the mineral will remain as potassium silicofluoride. This being a gelatinous compound, it is likely to enclose fine particles of the fusion and prevent their solution. If the amount of silica is not large, a separation may usually be effected by treating with concentrated hydrofluoric acid; but if much silica be present it is safer to evaporate to dryness with a little sulphuric acid, and take up the remaining potassium sulphate with water. If any insoluble substance is left it may be dissolved in hydrofluoric acid and added to the main portion of the solution.

If an analysis of the mineral is desired, hydrogen sulphide gas may now be passed through the acid filtrate, whereby any tin, tungsten, or molybdenum present will be precipitated as sulphide. Filter, and separate as usual.

The filtrate was evaporated to dryness, and enough sulphuric acid added to expel all the hydrofluoric acid. The excess of acid was driven off on an iron plate, not over a free flame, and the oxides of columbium, tantalum, and titanium precipitated

by boiling with a large quantity of water. The boiling must be continued for several hours to insure a complete precipitation, but it is not so difficult to bring down the metallic oxides under these conditions as in the bisulphate decomposition. Filter, and wash the oxides with hot water, first by decantation, then on the filter. The ignition of the oxides gave a *perfectly white*, fine powder; and this fused with sodium carbonate or potassium fluoride yielded a colorless mass when cold. The oxides obtained from the bisulphate never did so, but formed with the carbonate a tinge of green, and with the fluoride a tinge of pink, showing the presence of manganese and probably of iron.

The filtrate from the mixed oxides contained iron, manganese, and uranium. These were separated by ammonium sulphide and ammonium carbonate, following the plan given under the bisulphate method.

When the object is simply the extraction of pure mixed oxides, the above procedure may be somewhat varied. The fusion is made just as usual, then taken up with water insufficient for perfect solution, and a small quantity of hydrofluoric acid, boiled, and filtered. On cooling, the filtrate will be found to be an almost solid mass of the columbium double fluoride, $2KF.CbOF_3.H_2O$, which separates as a beautiful shining salt and consists of thin laminæ. At first the tantalum double fluoride remains undissolved, or is dissolved only in small quantity, as it is a very insoluble salt compared with the columbium compound, but if too much hydrofluoric acid is added the tantalum will be discovered with the columbium potassium fluoride, and larger amounts of iron and manganese will also contaminate it. From a very concentrated solution of the columbium double fluoride, such as would be obtained by this method, any tantalum double fluoride will, if present, separate almost immediately. These needles should be examined under a microscope for the thin transparent plates of the columbium salt. When these begin to appear, filter at once and use a pump. The plates are a good indication that all tantalum is separated. The filtrate, on standing, will usually give the columbium salt, but it may have to be concentrated a little. The first crop of crystals may be colored pink by manganese or iron. Recrystallization, how-

ever, removes this. The next crop is fairly pure. When working with large quantities, a very satisfactory approximate separation of columbium from tantalum may be obtained by this method of extraction.

As boiling with pure water, or even with wâter containing a small amount of hydrofluoric acid decomposes the tantalum potassium fluoride and leaves an insoluble compound,

$$2(2KF.TaF_6)Ta_2O_5,$$

while the columbium double salt is practically unaffected, this treatment leaves us in the end a white, finely divided mass, which is almost free from columbium. By heating this residue on a water-bath with a rather concentrated solution of hydrofluoric acid and a little potassium fluoride, the tantalum potassium fluoride is obtained and may be purified by recrystallization.

The Gibbs method was used for the preparation of rather large quantities of tantalum and columbium potassium fluorides. I think it preferable to the bisulphate decomposition and subsequent solution of the oxides in hydrofluoric acid, in that it does not consume so much time, and iron and manganese are more readily eliminated. The only objection is that large platinum vessels are needed; as a substitute for these, rubber beakers and funnels were sometimes used.

The method finally adopted is as follows:

Separation of Columbium and Tantalum by their Potassium Double Fluorides.—The pure mixed oxides were placed in a platinum crucible with three times their weight of potassium fluoride, then moistened with hydrofluoric acid as described under the decomposition of the mineral by the Gibbs method. By treating the fusion with water and hydrofluoric acid an almost perfect solution was obtained since only a trace of silica was present. Concentration gave the long pointed needles of tantalum potassium fluoride, $2KF.TaF_5$. These were filtered and the solution again concentrated. The crystal crop should be examined under the microscope as it may be a mixture of tantalum and columbium. Usually it is only tantalum.

If a considerable excess of hydrofluoric acid and potassium

fluoride is present in the mother-liquor, the next crop of crystals may be a complex mass about which the analyst can come to no definite conclusion. The fraction consists principally of long crystals much like the titanium double fluoride, and to make the matter more puzzling these crystals are not so soluble as those separating at the same time. They may be obtained pure by treating the mixture with a few drops of water and quickly filtering. Recrystallization from pure water gives the laminated salt $2KF.CbOF_3.H_2O$. If the acid and potassium fluoride are not in large excess, usually two, and sometimes three, crops of the laminated salt are formed, but in time the long needles are almost sure to make their appearance. These needles were tested for titanium, but no satisfactory evidence of its presence was obtained.

When the solution is very concentrated large, thin plates separate from it. These do not give the reaction with gallotannic acid, but they react with zinc, hydrochloric acid, and potassium thiocyanate. This test for columbium compounds will be noticed later. Recrystallization does not give the laminated salt. The crystals are always found, and by no means in small quantity. With zinc and hydrochloric acid they give a greenish color which quickly becomes brown. They were repeatedly recrystallized, then decomposed with sulphuric acid. The oxide obtained was white and at 19° C. had a specific gravity of 4.57.

The oxide was placed in a platinum retort connected with a platinum condenser; hydrofluoric acid was poured over it and a free flame was applied. The volatile products were collected in water in a platinum dish. Several evaporations were necessary for the volatilization of this oxide. The solution in the dish was then treated with a small quantity of potassium fluoride and concentrated. The same large, thin plates crystallized out. These crystals were very beautiful, being frequently over an inch in length and one-half inch in width. They were so transparent that often their presence in the dish was altogether unnoticed.

ANALYSIS.

Substance taken. gram.	K_2SO_4 found. gram.	Cb_2O_5 found. gram.
0.5000	0.5268	0.0059

This analysis would indicate that the salt is probably acid potassium fluoride with a smalll quantity of the double fluoride of columbium, yet it must not be forgotten that the reactions given above cannot be regarded as conclusive evidence of the presence of columbium.

Because of the brown color with zinc and hydrochloric acid these crystals were also tested for titanium. Its presence could not be detected.

QUALITATIVE REACTIONS.

Throughout this investigation the following questions constantly arose : How shall the purity of the columbium and tantalum compounds be determined? When is columbium free from tantalum? When is it free from titanium?

In the earlier work upon columbium we find Hermann describing a new element which he obtained from the mother liquors of the columbium potassium fluoride. This element, he states, gave a dark brown solution when reduced with zinc and hydrochloric acid, while the pure columbium compound gave a blue color. Both these solutions on standing in the air reverted to the white hydrate. Marignac replied that the brown color was not due to ilmenium but to titanium, a view which is now generally accepted.

He also declares that a brown color is produced when the potassium columbium oxyfluoride is treated with zinc and hydrochloric acid, the acid being in considerable excess. Then by titrating with permanganate he found that an intermediate oxide had been formed, to which he gave the formula Cb_2O_4.

Crystals of the columbium salt, prepared as described above, continued to give this brown solution even after they had been subjected to five or six recrystallizations. Following the plan of Krüss and Nilson[1] the atomic value of the oxide contained in such crystals was determined by decomposing with sulphuric acid, weighing the pentoxide and the potassium sulphate, then

[1] *Ber. d. chem. Ges.*, **20**, 1676.

by the ratio $2K_2SO_4 : Cb_2O_5$ determining the value for Cb^V. This was found to be 85.7 Iron and manganese had been eliminated; titanium, therefore, was the probable cause of this low atomic value. The salt used was perfectly white, yielding a pure white oxide. The oxide was tested for titanium by the most delicate reactions known for the metal, but its presence could not be proved by any of them.

1 Color and Reduction Reaction. It has been found that the qualitative tests given in the various text-books for these three elements do not always hold good when the solution used is a double fluoride. As it is in this form that the separations are usually made, it has been thought advisable to note the action of some of the common reagents on these salts.

Gallotannic acid, which is considered the most characteristic test for columbium salts, behaves differently with different double fluorides. An acid solution of the laminated salt gives almost instantly, a deep, brick-red precipitate. The salt crystallizing in long needles gives a lighter red precipitate which does not separate so rapidly. The large, thin, transparent plates previously mentioned, give only a slight precipitate, and this is yellow in color. These reactions are most delicate if the salt be dissolved in water, a drop of hydrochloric acid added, then a little gallotannic acid dissolved in alcohol. After standing several hours all the precipitates assume the same color—a dark, brick red.

Tantalum double fluoride gives a sulphur yellow color with gallotannic acid. This, however, on standing becomes brick red, as the columbium does.

Titanium compounds are said to give a brownish color with gallotannic acid which changes quickly to an orange red. The potassium titanium fluoride gave a straw yellow color with this reagent; in time a flaky precipitate forms, but the color does not materially alter.

The following color reaction serves for the detection of very small quantities of columbium, and is applicable to any soluble columbium compound. An excess of potassium thiocyanate is added to a small quantity of the dissolved substance; then some pieces of zinc followed by strong hydrochloric acid. At

once the solution becomes a bright golden brown, which if much columbium be present may be almost red. A brisk and continued evolution of the gas does not alter this tint which is also stable for more than twenty-four hours in the acid solution. Neither titanium nor tantalum give any reaction with potassium thiocyanate under the above conditions.

Hyposulphurous acid, H_2SO_2, gives noteworthy color reactions with these salts. The tests were conducted in the following manner: A few cubic centimeters of a concentrated solution of sulphur dioxide were placed in a test tube provided with a cork, and granulated zinc was added. The liquid changed to a greenish color, and hydrogen was liberated. As soon as the evolution of the gas had ceased the solution containing the hyposulphurous acid was poured into the salt solution to be tested.

A solution of titanium double fluoride gave an orange yellow color at once. The oxide when treated in like manner became yellow.

Columbium double fluoride gave no color, but a white hydrate was soon precipitated. Columbic oxide gave a slight yellow tinge.

Tantalum double fluoride gave no color, but after standing a white precipitate separated. Tantalic oxide remained colorless when treated with hyposulphurous acid.

The white precipitates from the tantalum and columbium salts were probably hydrates due to the oxidation of the acid and its consequent action upon these salts.

Zinc and hydrochloric acid gave no reaction with the double fluoride of tantalum. With titanium a clear, delicate green was obtained. The columbium salts always gave a color with these reagents. The solution is at first dark blue, then a greenish brown, and finally a dark brown. Frequently a brown precipitate separates which on standing becomes white.

The hydrochloric acid solution of columbic oxide, and also the potassium columbium fluoride, were tested with hydrogen peroxide, this being accepted as one of the most delicate reagents for titanium. No yellow color in either case was obtained.

2. *Reactions with Wet Reagents.* A number of the ordinary reagents have been tried with these salts, the results being given in the following table. The reactions for the greater number are very different when the metal tested is as double fluoride. The ferrocyanides, in particular, have quite abandoned their ordinary colors with these compounds.

	$2KF. CbOF_3.H_2O$.	$2 KF.TaF_5$.	$2 KF. Ti F_4$.
Lead acetate.	White precipitate.	White precipitate.	White precipitate.
Mercuric chloride.	Slight precipitate in 24 hours.	Yellowish green precipitate.	Yellowish green precipitate.
Mercurous nitrate	Yellow precipitate		Precipitate soluble in water.
Potassium chromate.	White precipitate, soluble in H_2O. Party soluble in K_2CrO_4 solution		
Potassium bichromate.		Precipitate after standing.	
Potassium cyanide	White precipitate on boiling.	White precipitate.	White precipitate.
Potassium ferrocyanide.	Green blue precipitate on boiling.	Yellow precipitate on boiling.	Precipitate on boiling.
Potassium thiocyanate.	White precipitate.	White precipitate, soluble in the cold. Comes down by boiling.	
Potassium iodide.	White, granular precipitate. Iodine is liberated	White granular precipitate.	No precipitate, but iodine is liberated.
Disodium hydrogen phosphate.		White precipitate after standing.	White precipitate.
Silver nitrate.		White precipitate after standing.	
Sodium bisulphite	White precipitate.	White precipitate.	White precipitate.
Sodium pyrophosphate.		Slight cloudiness.	Precipitate.
Hypophosphorous acid.			Precipitate.
Sodium metaphosphate.		Slight cloudiness.	
Potassium bromide.	White precipitate.		

Disodium hydrogen phosphate, when added to titanium double fluoride, precipitates the titanium completely. The filtrate tested with ammonium hydroxide gave no precipitate. Columbium double fluoride, on the contrary, is not affected by this reagent.

After boiling a long time in a platinum dish a few white flocks were observed in the solution, but in such small quantity that they were disregarded. Whether this behavior may or may not be made the basis of a separation of these two elements is not yet determined, because of the difficulty in getting rid of the phosphoric acid. Fusion with sodium carbonate, extraction with water, and subsequent precipitation by sulphuric acid gives a mixture of sodium salt and columbic oxide. Some columbium remains in solution. Fusion with potassium acid sulphate is more satisfactory, yet is not complete.

DEPORTMENT OF TANTALUM, COLUMBIUM AND TITANIUM DOUBLE FLUORIDES TOWARD THE ELECTRIC CURRENT.

1. A solution of potassium columbium double fluoride, $2KF.\ CbOF_3.\ H_2O$, in water, was treated with a small amount of sodium acetate. The precipitate formed was dissolved in acetic acid, and through this solution a current of one ampere, obtained from a thermopile, was conducted for five hours. A white precipitate, seemingly a hydrate, was formed. On breaking the current this rapidily went into solution.

2. (*a*) A solution of the salt in water was subjected to the same current for eight hours. Almost immediately the bottom of the platinum dish was covered with a blue deposit. This gradually spread over the whole surface exposed to the action of the current, and became in a short time iridescent. As the deposit increased, the deep blue tint changed to more of a gray, and remained so until the current was broken. It was washed quickly with water, then with alcohol, and it was dried on the hand.

0.1315 gram of the salt was taken; the deposit weighed 0.0282 gram. This metallic looking substance did not alter in the air, but on subjecting it to a red heat, a white, shining, apparently crystalline compound resulted. It was readily soluble in hydrofluoric acid.

(*b*) A second experiment, with 0.2195 gram of the substance, gave under the same conditions, a deposit weighing 0.0388 gram. This when ignited in the air burned to a white oxide weighing 0.0312 gram. The blue compound is in all probability, a lower hydrated oxide of columbium.

3. The electrolysis of an aqueous solution of a sodium columbate gave a white, flucculent hydrate, not adherent to the dish. The precipitation was not complete. A current of one ampere was employed for a period of seven hours.

4. With a much stronger current (two amperes), a solution of the double salt $2KF.\ CbOF_3.\ H_2O$, gave first a white hydrate, then beneath the outer edge of the anode appeared a dark brown ring which gradually grew in toward the center of the dish, never reaching it however, but stopping when about half an inch in width.

This brown substance was slightly adherent to the dish, but just as soon as the current was broken, and the liquid poured off, it reverted to the white hydrate. This change was so rapid that it was impossible to separate the brown from the white substance.

Thinking that this brown compound might be a contaminating element, about one gram of the double salt was dissolved in water and electrolyzed until the brown ring had appeared. Then the liquid was poured into another dish as quickly as possible, and the current run through again. The brown ring appeared as before, and was treated in the same manner. After changing the dish four times only a trace of brown could be seen. When the remaining solution was evaporated it was found that almost the entire quantity of the columbium had been precipitated. The brown substance here formed resembles in its behavior that produced in a like solution by zinc and hydrochloric acid.

The resistance of this solution is very high.

5. Potassium tantalum fluoride in aqueous solution was subjected to the action of a current of two amperes for six hours. A small quantity of hydrate was found in the liquid and on the dish a very slight iridescent deposit mixed with some white hydrate.

6. Potassium titanium fluoride was treated in the same manner as the previous salt. A small quantity of hydrate was found here, some of which adhered to the dish. The iridescent deposit, however, was wanting.

ACTION OF HYDROFLUORIC ACID UPON THE OXIDES OF TANTALUM, COLUMBIUM, TITANIUM, AND SILICON.

The well known volatility of the oxides of tantalum and columbium when heated with hydrofluoric acid led to the hope that in this behavior might lie a separation from titanium and also from silica.

Rose states that a very appreciable loss occurs when the first two oxides are treated as suggested, but he makes no attempt to separate them from the latter two. To this end one gram of the mixed oxides of tantalum and columbium was evaporated to dryness with hydrofluoric acid, the residue being heated over the free flame for a few minutes. By this treatment dense white vapors were driven off. Upon weighing the residual oxides they were found to equal 0.5464 gram. A second evaporation gave further loss, but as both columbium and tantalum continued to remain, the method is without value.

The separation of silica from these oxides can be accomplished by the heat of an iron plate after evaporating to dryness on a water bath. The final heating must be carefully done, and the acid should not be in too great excess.

I have never found it impossible to dissolve either the mixed or the pure oxide in hydrofluoric acid, even though strongly ignited. It is true, concentrated acid is necessary, and a little time is often required, but a perfect solution does take place.

Tantalic oxide, containing columbic oxide, is far more soluble in hydrofluoric acid than the pure oxide. The same behavior has been observed with pure columbic oxide, though it is not so pronounced as with tantalic oxide. Titanium dioxide, ignited, is very difficultly soluble in this reagent, though columbic oxide, containing titanic oxide, went quickly into solution.

DOUBLE FLUORIDES OF TANTALUM, COLUMBIUM, AND TITANIUM, WITH RUBIDIUM AND CESIUM.

The potassium double fluorides of tantalum and columbium have been found of great service in separating these two metals. Marignac first showed that a separation could be effected through these salts, and he also demonstrated that the sodium and ammonium salts were inapplicable.

Of the potassium double fluorides of tantalum and columbium we possess considerable information. A number have been isolated and studied. The sodium salts crystallize so poorly that their history is not so well known. It seemed probable that rubidium and cesium would form double fluorides of definite crystalline character with these three metals. At least, a study of their behavior might be found instructive. Before taking up their preparation, however, the simple fluorides of rubidium and and cesium may be discussed.

Rubidium Fluoride (RbF).—An examination of the literature on rubidium showed that its fluoride had not been prepared. In order to procure this, rubidium iodide was dissolved in water and moist silver oxide added to precipitate the iodine. The solution of rubidium hydrate resulting, was filtered off and evaporated in porcelain dishes. A very appreciable quantity of silver oxide was held in solution by the rubidium hydroxide, so that it was necessary to evaporate it almost to dryness, then to take it up in the smallest possible quantity of water and filter. This treatment may have to be repeated two or three times before the solution is perfectly colorless. When quite free from silver, the concentrated solution was made slightly acid with hydrofluoric acid, and evaporated. If hydrofluoric acid be present it is almost impossible to obtain crystals, a thick syrup being formed which defies all attempts in that direction. The solution is therefore evaporated with water several times until the excess of acid is expelled. The rubidium fluoride then crystallized in long, transparent plates. These were drained, and dried between filter paper. The salt was anhydrous. Conversion into sulphate by evaporating with sulphuric acid gave, from 0.5 gram of the salt, 0.5236 gram rubidium sulphate. This corresponds, therefore, to the formula RbF.

Cesium Fluoride.—Cesium chloride was dissolved in water, and the chlorine precipitated by moist silver oxide. The solubility of the oxide of silver in cesium hydrate is even greater than in rubidium hydrate, therefore some difficulty was experienced in obtaining a hydrate free from silver. It was finally accomplished by evaporating to dryness repeatedly, taking up the cesium hydrate in a very small quantity of water and filter-

ing it. The pure hydrate was then neutralized with hydrofluoric acid and evaporated. A thick syrup was obtained, which refused to crystallize. Upon heating in an air bath to 130° C., a crystalline mass formed, but it was always in such a sticky condition, and absorbed moisture so rapidly, that it could not be analyzed satisfactorily. This mass was dissolved in water and added to the solutions of the metals in hydrofluoric acid.

Double Fluoride of Columbium and Rubidium.—One-half gram of columbic oxide was dissolved in hydrofluoric acid and the calculated quantity of rubidium fluoride added. The solution was evaporated on a water bath to expel the excess of acid. The residue was taken up in hot water and allowed to crystallize spontaneously. White microscopic plates separated. These were filtered off, dried between filter paper, and analyzed. Two-tenths gram of the dry salt gave

	Found.	Calculated for $2RbF.CbF_5$.	Difference.
Cb_2O_5	0.0670	0.0673	—0.0003
RbF	0.1048	0.1049	—0.0001

The formula of the salt is therefore, $2RbF.CbF_5$, corresponding to the tantalum salt usually obtained with potassium fluoride.

The filtrate from this first crop of crystals was slightly concentrated, when small, shining, or even iridescent crystals, apparently plates, separated. Upon standing a short time these changed over into crystals like those first mentioned. This salt is very soluble in water containing hydrofluoric acid, and also in pure water. It is insoluble in alcohol.

Double Fluoride of Rubidium and Tantalum.—Rubidium fluoride in slight excess was added to tantalic oxide dissolved in hydrofluoric acid. Small white needles crystallized out. An excess of acid must be present, otherwise heat decomposes the double salt, giving a fine, white, insoluble compound, as is the case with the potassium salt.

Analysis of two-tenths gram gave

	Found.	Calculated for $2RbF.TaF_5$.	Difference.
Ta_2O_5	0.0915	0.0913	+0.0002
RbF	0.0861	0.0859	+0.0002

Double Fluoride of Titanium and Rubidium.—The preparation

of this salt was conducted as described with preceding salts. The crystals here were also microscopic needles. Some difficulty was at first experienced in completely drying the salt, but this was overcome by several recrystallizations from pure water, when an anhydrous product was obtained. One-tenth gram of the salt gave on analysis

	Found. Gram.	Calculated for $2RbF.TiF_4$. Gram.	Difference.
TiO_2	0.0238	0.0240	—0.0002
RbF	0.0622	0.0626	—0.0004

Double Fluoride of Tantalum and Cesium[1].—This double salt was formed by the addition of a solution of the cesium hydrate in hydrofluoric acid to a solution of tantalic oxide in hydrofluoric acid. Very beautiful white needles separated, which were not easily soluble in water, and were not decomposed by recrystallization from pure water. The aqueous solution may be evaporated on a water-bath with perfect safety, this being apparently much more stable than either the potassium or rubidium salt.

The crystals were dried in the air, then heated to 125° C. in an air-bath. No loss in weight was observed. 0.25 gram gave on analysis

	Found.	Calculated for $15CsF.TaF_5$.	Difference.
Ta_2O_5	0.0212	0.0217	—0.0005
CsF	0.2232	0.2228	—0.0004

The formula deduced from the analytical data varies widely from that generally followed by tantalum double fluorides. Neither is it in accordance with Remsen's law for the double halides[2] though it will be observed that its fluorine content bears a simple ratio to the fluorine in combination with the tantalum.

Double Fluoride of Columbium and Cesium.—This double salt was formed in the manner described for the preparation of the cesium tantalum fluoride. It is very soluble in water containing hydrofluoric acid, and in pure water, from which it crystallizes in needles. These when pure are anhydrous. Boiling

[1] This and all the other cesium double fluorides are being subjected, at this writing, to further study in this laboratory. EDGAR F. SMITH.

[2] *Am. Chem. J.*, 2, 291.

with pure water does not decompose the salt. Analysis of two-tenths gram gave the following result:

	Found.	Calculated for $7CsF.CbF_5$.	Difference.
Cb_2O_5	0.0216	0.0213	+0.0003
CsF	0.1694	0.1698	−0.0004

This salt, which appears to be $7CsF.CbF_5$, is even more erratic in its constitution than the tantalum cesium compound. There is apparently no relation here between the fluoride in combination with the columbium and the number of molecules of cesium fluoride present.

Double Fluoride of Titanium and Cesium.—This salt separates in very small shining crystals when cesium fluoride is added to a rather concentrated solution of titanic oxide in hydrofluoric acid. It is more readily soluble in water than the tantalum cesium compound, and is not decomposed by pure water. The air dried crystals showed no loss in weight after heating for some time at 125° C. An analysis of 0.25 gram gave the following amounts of titanic oxide and cesium fluoride:

	Found.	Calculated for $4CsF.TiF_4$.	Difference.
TiO_2	0.0269	0.0271	+0.0002
CsF	0.2071	0.2076	−0.0005

The figures point to the formula $4CsF.TiF_4$. This is a departure from the usual titanium double fluorides, and agrees with the law laid down by Remsen for these salts.

When we consider the atomic masses of tantalum, columbium, and titanium, the first 182, the second 94, and the third 48, and also consider the quantities of cesium fluoride which unite with a molecule of each of the metallic fluorides, we find that with tantalum the quantity (fifteen) is nearly twice that with columbium (seven) and the latter almost double that (four) uniting with titanium, just as 182 is about twice 94, and 94 nearly twice 48.

These new cesium compounds tend to confirm the conclusions drawn by Wells and others[1] from their work on the cesium double halides. The compounds investigated by these chemists show that the cesium double halides are not wholly conformable to Remsen's law.

[1] *Am. J. Sci.*, 47.

The method of analysis pursued for the determination of these double salts is, briefly, as follows :

The dry substance was decomposed in a platinum crucible by a few drops of concentrated sulphuric acid. The hydrofluoric acid was driven off, and the excess of sulphuric acid was then expelled on a sand-bath. The temperature must be just sufficient to drive off the acid. The metallic oxide was obtained from the sulphate by long boiling with a large quantity of water. It was then filtered, washed about twenty times with boiling water, ignited, and weighed. The filtrate, containing the alkaline sulphate, was evaporated, the excess of acid neutralized with ammonium carbonate, and the solution then evaporated to dryness on a water-bath A saturated solution of ammonium carbonate was added, and the mixture evaporated again to dryness. The ammonium salts were expelled by careful heating. Constant weight can generally be obtained after two or three evaporations with ammonium carbonate. The rubidium sulphate decrepitates on heating, which necessitated great care while expelling ammonium salts, and also rendered the method proposed by Krüss (heating in a stream of ammonia gas), untrustworthy. The alkalies were then weighed as normal sulphate, and the cesium or rubidium content calculated. This method, while slow, has been found very satisfactory for these rare alkalies.

PRODUCTS OBTAINED ON HEATING THE OXIDES OF TANTALUM AND COLUMBIUM WITH PHOSPHORUS PENTACHLORIDE.

One-half gram of columbic oxide was heated with phosphorus pentachloride, the quantity being calculated from the following equation :

$$Cb_2O_5 + 5PCl_5 = 2CbCl_5 + 5POCl_3.$$

The experiment was conducted in a sealed tube from which all air had been expelled, the temperature being maintained at 180°–200° C., for seven hours. The resulting mass was moist, and a dirty green. The tube was opened, connected quickly with a small test tube, and then heated in an air-bath. A small quantity of liquid distilled into the front part of the tube. This was a yellowish green, and gave with water a white precipitate, apparently a hydrated columbic oxide.

At a higher temperature, about 200° C., yellow vapors collected in the cool portion of the tube. These settled on the glass as yellow, oily drops, and on cooling solidified, long yellow needles being detected here and there. Nearly all of the substance in the tube, however, remained as the greenish mass, which had become dry. No change was observed on heating above 360° C. The tube was then wrapped in copper gauze and heated with a Bunsen lamp. The green substance swelled up, became white, iridescent, and almost filled the tube. No green color remained. Analysis of this compound showed it to be columbium oxychloride, $CbOCl_3$. The long yellow needles which had been observed in the front part of the tube changed gradually on heating, and became white and iridescent like the remainder of the substance.

This behavior indicated the formation of a pentachloride, which was then changed to oxychloride by the small quantity of air which entered the tube when it was connected with the receiver.

A second tube, heated for eight hours at 230°–235° C., gave a dark yellow, semi-fluid mass. Great care was taken in this experiment to exclude all traces of moisture, and the distillation was conducted under reduced pressure. Phosphorus oxychloride in considerable quantity distilled over, leaving in the tube a yellow crystalline substance, which, on treating with water, decomposed with hissing and an evolution of hydrochloric acid gas. This compound was analyzed according to the method of Marignac.[1] The ignited oxide weighed 0.5642 gram. As only one-half gram of columbic oxide was used in the experiment, the contaminating substance was sought, and was found to be phosphorus. Two fusions with bisulphate were necessary for the extraction of this element. Phosphoric acid was also found in the filtrate from the pentoxide.

The question now arose regarding the position of this phosphorus: Is there a compound formed containing columbium, phosphorus, and chlorine, or is the phosphorus content due to an incomplete expulsion of the excess of phosphorus pentachloride?

[1] *Ann. chim. phys.*, 8, 5.

Another experiment was therefore tried under the following conditions: One-half gram columbium pentoxide was heated with the calculated quantity of phosphorus pentachloride at a temperature not exceeding 210° C. for eight hours. The tube contained a yellow mass as before. It was placed in an air-bath and connected with a chlorine generator, the receiver having been previously filled with chlorine. At 190° C. a very volatile substance collected in the front part of the receiver. This was a lemon yellow, and when analyzed gave 15.85 per cent. columbium and 6.095 per cent. phosphorus.

At 190°–200° C., long yellow needles collected; some of these were nearly half an inch in length. Analysis gave 27.37 per cent. columbium and 32.19 per cent. phosphorus.

The substance which did not volatilize at 200° C. was brownish-yellow, and apparently crystalline. Analysis gave 28.11 per cent. columbium, and 1.34 per cent. phosphorus.

In none of these analyses could the chlorine content be determined, because of the violence with which water acts upon the compounds, resulting invariably in the loss of some hydrochloric acid.

It seemed probable that the brownish-yellow residue in the tube was columbium pentachloride, enclosing a small quantity of phosphorus pentachloride. To determine all three elements, the following method was used:

The more volatile compounds having been removed by distillation in a stream of chlorine gas the residual substance was quickly weighed and thrown into a dilute solution of silver nitrate. The precipitate of silver chloride, silver phosphate, and hydrated columbic oxide was then filtered, and washed on the filter with dilute nitric acid. The phosphoric acid obtained was determined by a magnesium mixture. Dilute ammonium hydroxide was then poured over the mixture of silver chloride and columbic oxide. It was found that all the silver salt could not be removed by this means. The mixture was therefore transferred to a porcelain crucible and reduced in a stream of hydrogen gas, the metallic silver being dissolved out with dilute nitric acid, then precipitated as chloride. The columbium remained

in the form of a violet compound, which on ignition in the air went over to pentoxide.

A small quantity of phosphorus was obtained, which was calculated into pentachloride and deducted from the material taken.

Rose states that a columbate of silver, $Cb_2O_5.Ag_2O$, is formed on the addition of silver nitrate to a solution of sodium columbate. As, upon the addition of water to columbium pentachloride, an almost perfect solution is produced for a few moments, the columbium in solution may combine with the silver. In such a case the silver chloride finally weighed would represent both the silver in combination with chlorine and that with columbium.

The analytical results are as follows:

Substance taken = 0.8917 gram.
Phosphorus found = 0.02596 gram.

This, as phosphorus pentachloride, requires 0.14829 gram of chlorine.

Substance taken minus PCl_5 = 0.7175 gram.
Columbium found = 0.2485 gram.
Columbium required = 0.2484 gram.
Chlorine found = 0.66509 gram.

Taking from this 0.14829 gram of chlorine, which is in combination with phosphorus, we have chlorine = 0.5168 gram; columbium pentachloride requires 0.4691 gram. Calculating the quantity of silver which, according to Rose's formula, would combine with the amount of columbium oxide found, and deducting the chlorine corresponding to it, 0.4699 gram of chlorine is found to be in combination with the columbium.

The volatile compounds mentioned above were recalculated into phosphorus pentachloride and columbium pentachloride. It was found that by removing the phosphorus as pentachloride satisfactory analyses for columbium pentachloride were obtained from the residues.

Tantalic oxide was also heated with phosphorus pentachloride, the same conditions being maintained as in the columbium experiments. A yellow mass was formed lighter in color than the columbium compound, and only slightly moist. The tube was placed in an air-bath and distilled at a temperature not exceeding 245° C. This distillation was conducted under

reduced pressure. A small quantity of phosphorus oxychloride distilled over, and in the front part of the tube a little phosphorus pentachloride collected. The tantalum compound remaining was light yellow, dry, and powdery—apparently amorphous. It combined with water with hissing, liberating tantalic oxide, which contained no pnosphorus. A small quantity of this element was found in the filtrate from the oxide. It was calculated into phosphorus pentachloride, and deducted from the total quantity.

Weight of substance taken = 0.6700 gram.
Weight of tantalum found = 0.3389 gram.
Required tantalum = 0.3391 gram.

Tantalum pentachloride is, therefore, formed when tantalic oxide is heated with phosphorus as pentachloride.

REDUCTION OF THE COMPOUNDS OF COLUMBIUM AND TANTALUM TO METAL.

Two experiments aiming at the preparation of columbium and tantalum in the metallic state have been tried during this research, and I regret exceedingly that the lack of time has prevented a more careful study of the reactions obtained. It is my intention to go more deeply into the subject than I have been able to do.

Experiment 1. An iron cylinder, three inches in diameter, having an inch bore, was charged in the following manner: First, a layer of dry salt, than a layer of metallic sodium, above which were placed about seven grams of potassium tantalum fluoride, this being followed by another layer of sodium. The cylinder was then tightly packed with dry salt, and a heavy lid screwed on. It was then placed in a wind furnace, the temperature of which was comparatively low. In less than one-half hour it was found that the cylinder had melted down, and no trace of the charge could be found.

Experiment 2. Marignac obtained an alloy of columbium and aluminum by heating the potassium double fluoride with aluminum scales in a carbon crucible. In the experiment to be described columbic oxide was used, salt and cryolite being employed as a flux. The following layers were placed in a graphite crucible:

1. Salt.
2. Cryolite.
3. Aluminum clippings.
4. Columbic oxide.
5. Aluminum clippings.
6. Cryolite.
7. Salt.

The proportions of these substances used were:

2 parts Cb_2O_5.
10 parts cryolite.
15 parts aluminum.
x parts sodium chloride.

The graphite lid was firmly luted on with fire-clay, the crucible was buried in a wind furnace which was kept at a white heat for eight hours. At the end of this time it was found that the graphite crucible had been severely attacked. It was reduced to a shapeless mass, but on breaking, a powdery substance was found, in which were contained many little metallic buttons varying in size from a large pea to those of microscopic proportions. These were carefully picked out, and various reagents tried upon them.

Single acids do not attack them. Aqua regia makes a slight impression on long heating. Fusion with bisulphate affords only a partial decomposition. The substance is exceedingly light, it is dark gray, and does not alter in the air. A partial oxidation occurs after prolonged heating in the air. The substance is not brittle.

SUMMARY.

1. The decomposition of columbite is more readily and satisfactorily accomplished by the Gibbs than by the bisulphate method. This method is also more valuable for the preparation of large quantities of pure oxides.

2. The qualitative reactions of columbium, tantalum and titanium when existing as double fluorides are not the same as when the metals exist as tantalates, columbates and titanates.

3. The action of the electric current upon tantalum and columbium double fluorides gives a lower hydrated oxide. The precipitation is not complete.

4. It was hoped that in preparing the double fluorides of

columbium, tantalum and titanium with rubidium and cesium a difference in solubility of the salts would be found which would afford a better separation of these metallic oxides under discussion. This hope has not been realized.

5. Heating the oxides of columbium and tantalum in sealed and vacuous tubes with phosphorus pentachloride yields the pentachlorides of these metals and phosphorus oxychloride.

I take pleasure in acknowledging the kindness shown, and the interest taken in the preceeding work by Dr. Edgar F. Smith, of this University, in whose laboratory it was carried out.

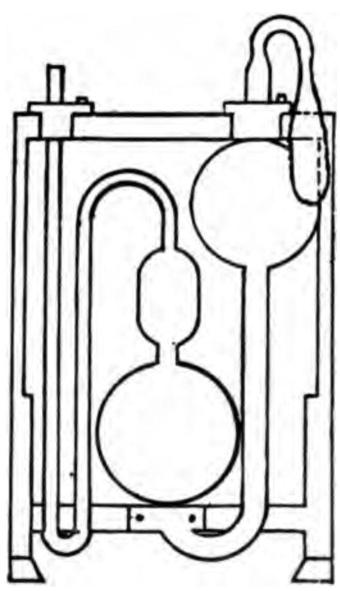
UNIVERSITY OF PENNSYLVANIA,
JUNE, 1895.

AN IMPROVED GAS PIPETTE FOR THE ABSORPTION OF ILLUMINANTS.

BY AUGUSTUS H. GILL.

Received October 12, 1895.

IN the use of the apparatus for this purpose ordinarily furnished by the dealers, difficulty has always been experienced in sucking the gas back from the pipette, owing to the moist beads and the glass wool entrapping some bubbles.



To obviate this, the writer has, for the past two years, made use of the modification shown at one-fourth size in the sketch. The round bulb filled with beads and glass wool in the usual form, is replaced by a cylindrical one about two inches long and an inch and a quarter in diameter, filled with tubes standing vertically, after the manner of the Orsat pipettes. The surface presented is nearly the same and no trapping of the gas can take place.

The stand is the one already described,[1] and the whole apparatus may be obtained of the Ziegeler Electric Co., of Boston.

[1] Gill: *Am. Chem. J.*, 14, 231.

THE COLORING-MATTER OF NATURAL WATERS, ITS SOURCE, COMPOSITION AND QUANTITATIVE MEASUREMENT.

By Ellen H. Richards and J. W. Ellms.

Received August 31, 1895.

SO deeply seated in the mind of the average citizen is the prejudice against the amber-colored water of the most of the New England streams that it is only when reinforced by scientific authority that water boards and city councils are able to make any impression upon it.

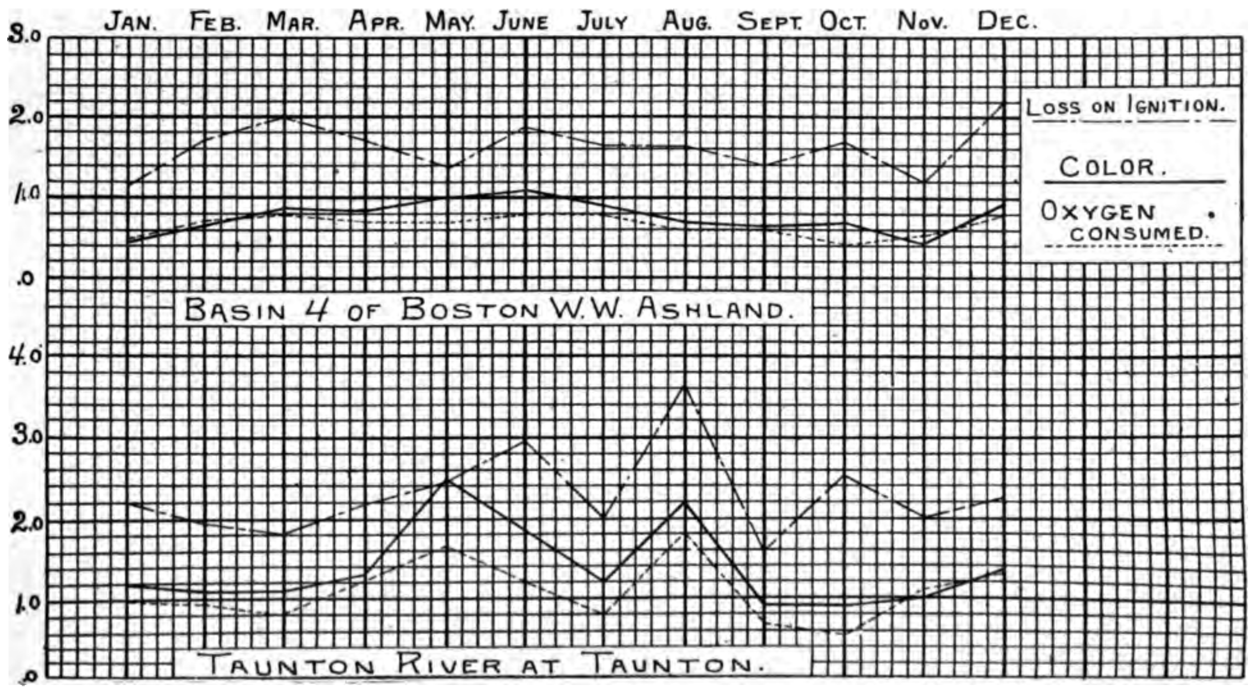
It is only by actually filling up the well or by taking out the pump, that any Board of Health can prevent the use of a clear, cold, colorless, highly polluted well-water, no matter how abundant and free the tepid, turbid brown water supplied from the tap.

Color seems to have been associated in the popular mind with all sorts of hidden dangers. There lingers yet in memory the echoes of stories told to childish ears of the agonies suffered by those deluded persons who, in spite of the warning of their elders, persisted in drinking from wayside brooks and thus unwittingly swallowed what grew to be living monsters within them.

While there must be some ground for so strong and universal a feeling of danger, experience has certainly shown that a brown water from a carefully protected water-shed, when properly stored, yields a perfectly wholesome as well as most available and abundant source of supply.

It is said that the water from the Dismal Swamp is sought for by sailing vessels to take for three year cruises and many other brown waters have shown excellent keeping qualities after being stored for a time in clean basins to allow of the sedimentation of the extraneous matter which may have been carried along by streams.

The source of brown color in natural surface waters is to be found in the decaying elm, maple, oak, and other leaves which carpet the hillsides and swamps each autumn, and in the surface soil, which everywhere, and particularly in the lowlands, is rich in peaty or "humus" matter.



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LOSS ON IGNITION.
COLOR.
OXYGEN CONSUMED.
BASIN 4 OF BOSTON W.W. ASHLAND.
TAUNTON RIVER AT TAUNTON.

CHART I.

The chlorophyl derivatives, glucoses, and glucosides dissolve out of the fallen leaves in the early autumn, giving a light yellow color to the brooks, but after soaking all winter, mostly under the ice and snow, the leaves yield to the warm spring rains a rich deep brown liquid which is exactly what Thoreau, with poetic instinct, called it, namely "meadow tea." It is at least as harmless as Japan tea. The coloring-matter in both cases is due to the slow carbonizing of the leaf and the formation of soluble compounds rich in carbon.

The variation in the depth of color of brown surface water at different seasons of the year, is well shown in chart 1. The color curve plotted for basin 4 of the Boston Water Works, in Ashland, for a year, shows the steady rise in color from January to June, and then a falling off toward the latter part of the year. This is a typical, unpolluted surface water. Taunton river, on the other hand, receives drainage from a variety of sources as well as from the neighboring swamps, and shows greater fluctuations.

When any organic substance as wood, leaves, and the like, is treated with strong sulphuric acid, a decomposition occurs more or less complete; and the result is, according to the strength of the acid and the temperature at which it is applied, either a mass of nearly pure carbon or a gummy substance soluble in water with the production of a deep brown-colored solution. When sugar is gently heated it parts with a portion of the elements of water, becoming richer in carbon as the process is pushed farther. The result is a brown substance known as "caromel" soluble in water; there also may be produced various less soluble compounds, depending on the temperature used, which have been at times called caramelane, caramelin, and caramelene.[1]

But the most instructive instance of the production of this characteristic brown substance is, perhaps, in the case of the well known colorimetric determination of carbon in steel. By using Stead's alkali method, a soluble brown color is obtained which compares very closely with the color of the dark brown waters under consideration. Whether an estimation of the

[1] Peligot, *Ann. chim., phys.* [2], 67, 172, Völckel, *Ann. Chem.* (Liebig), 85, 59: Maumené, *Compt. rend.*, 39, 422; Graham, *J. Chem. Soc.*, 15, 258.

actual quantity of carbon in these coloring-matters can be made, is yet to be determined.

The color in solutions from all these sources may be removed with milk of alumina, may be precipitated by barium hydroxide, and in all cases the solutions are decolorized by the action of potassium permanganate, indicating the complete oxidation of the color-giving compound of carbon. All are comparable in color when matched in tubes or read in the tintometer to be described.

These facts all indicate that this brown color is imparted to aqueous solutions by the same compound of carbon or by closely related compounds.

In the coloring-matter of surface waters there are, most probably, several complex substances, among them tannins, glucosides, and their derivatives, out of which it seems almost hopeless to attempt to isolate any one which may be said to be the substance under consideration. Some of these decomposition-products contain iron and it has been suggested that the color-giving compounds may result from the breaking up of chlorophyl.[1] That iron is not essential to the formation of the color is shown by the fact that the brown color may be given by a solution of caramel made from pure sugar, and that iron may be absent from the carbon color obtained from steel, but it is true that a very small quantity of iron does, as a rule, accompany the brown color of natural waters.

Since any colored natural water gives a certain proportion of albuminoid, ammonia, increasing as the color increases, it would seem that the color compound might contain nitrogen. The following are results of experiments tried some years ago :

	Color.	Albuminoid ammonia.
(1) Peat solution	2.0	0.0516
(2) Fresh leaf solution	0.8	0.0494
(3) Second extract of same leaf	0.8	0.0174
(4) An old leaf repeatedly extracted with water	0.9	0.0072

It will be seen in the two leaf solutions (2 and 3) with the same color of eight-tenths there is a reduction of 64.7 per cent. in the nitrogen and that with a color of one-tenth more in the

[1] F. S. Hollis, Report of the Boston Water Board, 1892.

old leaf solution (4) there is 85.4 per cent. less nitrogen than in the fresh leaf solution (2). While it is possible that the color giving compound or compounds contain nitrogen as an essential constituent, it is evident that a large diminution in the nitrogen does not produce a corresponding lessening of the color.

The following figures show the carbon, hydrogen, and nitrogen contained in (1) the residue of Boston tap water, (2) a very dark-colored water from Cedar Swamp, Westboro, and (3) humic acid extracted from soil.

	Carbon.	Hydrogen.	Nitrogen.
Boston tap water[1]	30.71	5.96	7.68
Cedar Swamp water[1]	43.72	3.92	4.82
Humic acid[2]	50.4	4.8	3.6

No attempt has been made by us to give a more definite formula for these apparently highly carbonaceous compounds since so little seems to be known of the reactions attending the gradual carbonization of such organic substances. It is probable that one of the compounds may be what is known to the agricultural chemist as humic acid or humus matter. Berthelot finds a close relation between this substance prepared from peat and from sugar, only the latter is free from nitrogen.

QUANTITATIVE MEASUREMENT.

Formerly the brown color of water was supposed to be a bar to its use for domestic purposes and analysts sought for some standard of comparison by which to set a limit of allowable color. One of the early methods was by the determination of the quantity of oxygen consumed or absorbed from potassium permanganate, either hot or cold in acid or alkaline solution. If the substance which gave the brown color had a known composition so that any given percentage of oxygen consumed could be said to correspond to a definite quantity of the carbonaceous compound, this might be a valuable standard. The fact is, however, that at present the results are often misleading, since a highly polluted water may give much lower results than a dark brown water which by years of use has been shown to be perfectly wholesome.

1 H. T. Gallup, Thesis, Mass. Inst. Tech., 1894.
2 Berthelot: *Compt. rend.*, 569, *1892*.

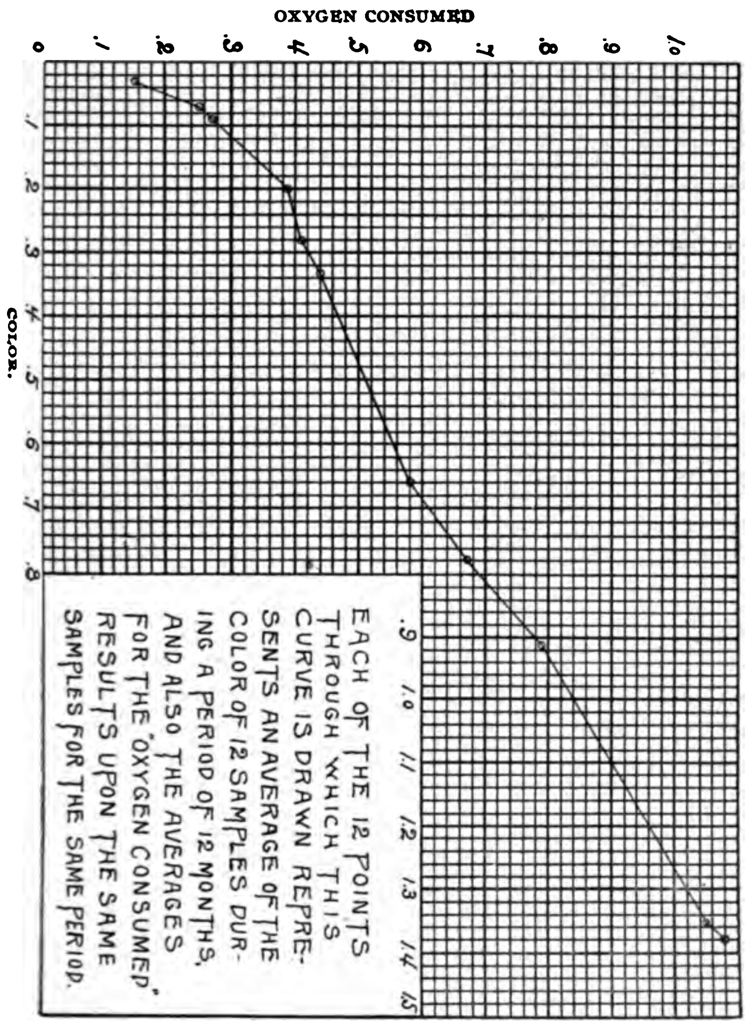


CHART II.

Since not all carbon compounds are affected by this treatment and since the organic matter in solution is probably made up of several substances having quite different composition it is not surprising that we have thus far failed to establish a definite relation between the quantity of organic matter present and the oxygen given up to it by the potassium permanganate. In a

general way, a rise in color is followed by a rise in the oxygen consumed, as is shown by the diagram on chart II.

As soon as the fact was recognized that fixed standards could not be rigidly applied to all waters from all sources, and that a certain quantity of albuminoid ammonia invariably accompanied the brown color of perfectly wholesome water and somewhat in proportion to the color,[1] it became of importance to be able to estimate the relative depth of color in waters. For this some standard was of course required. Various substances have been proposed from time to time, such as solutions of caramel, and metallic solutions[2] of various kinds. Largely on account of its convenience as being always in use in the laboratory and because the colors matched easily, the method orginally suggested by Prof. A. R. Leeds,[3] namely, the use of the nesslerized ammonia stundards, was at first adopted in the Laboratory for Water Analysis of the Institute of Technology.

It occurred to one of us[4] to prepare considerable quantities of water of the various depths of color most frequently met with in ordinary routine work, and to use these as standards of comparison, of course based upon the ammonia standards made with a Nessler solution which gave a sufficiently brown tint. An additional advantage to that of having them ready at a moment's notice was that the colors were identical and no mental effort was necessary to eliminate the slight differences in tint which almost of necessity occurs when two substances of unlike composition are compared.

Natural water standards when so prepared fade in time like the caramel solutions, even when carefully covered from the light, and, although sterilized at first, the bottles cannot remain so when opened for daily use, so that a freshly standardized set is required as often as once in six months. It is well known that the Nesslerized ammonia standards vary considerably as prepared in different laboratories because of the different methods of making up the Nessler solution, and it was very desirable

[1] T. M. Drown: The Interpretation of Analyses, Mass. State Board of Health Report 1890, p. 566.

[2] Crookes, Odling & Tidy: *Chem. News*, 43, 174; Hazen: *Am. Chem. J.*, 14, 300.

[3] Proceedings Am. Chem. Soc., 2, 8.

[4] Mrs. E. H. Richards, Mass. State Board of Health Report, 1890, p. 532.

to find some standards of absolute quantitative value, which could be applied anywhere, and which would give comparable results.

Many chemists have found the metallic standard of platinum and cobalt satisfactory for tests for the working of filters and where only low colors are dealt with; but for the wide range of colors met with in our work, some 500 numbers from 0.01 to 5.00 we cannot match two such different combinations of colors with any degree of accuracy in the higher portions of the scale.

The reason is evident, and it is equally patent in all forms of color measurement; "for color is not a simple physical quantity like weight of temperature, but a physiological effect which varies with individual peculiarities and bears no very simple relation to the physical causes which produce it."[1]

The constituents of the resulting matched colors also may be very different and one may vary more than the other under varying conditions of light, depth of column, and density.

There is a wide field for experiment in the physics of color-measurement in solution and which in view of the increasing use of such methods in quantitative determinations is of extreme importance to chemists. Without going into detail on this point, one instance may be cited. It has been observed in matching Nessler standards that the readings are exact only within certain limits; for instance, colors higher than those given by four cc. of standard ammonia, 0.00001 gram in one cc. observed in a column of nine inches in depth, are very difficult to compare, and as the quantity of ammonia increases the color becomes more and more red until the point of precipitation is reached. That is, the normal eye is more sensitive to certain shades of colors than to others and there is a limit to the depth of color which can be correctly estimated. Also, while one solution may appear redder than another in a deep column it may appear less red in another of a less depth. For example, a natural water standard of color, 5.0 on the Nessler scale contains only 0.0005 per cent. dissolved organic matter. A solution of carbon from steel, prepared by Stead's[2] method, is

[1] H. R. Proctor: *J. Soc. Chem. Ind.*, 14, 2.

[2] J. Iron and Steel Inst., 1883, p. 213; also Blair's Iron Analysis, p. 170.

strongly alkaline and contains twenty per cent. dissolved salts. A solution of caramel is nearly the same in character as the water, and strongly acid solution of platinum and cobalt contains two-tenths per cent. of salts. If these solutions are matched as nearly as bossible by the eye in nine-inch tubes and then the tintometer readings are taken, it is found that the ratio of orange to excess of yellow in the water standard is as one to 1.21, or the color is yellow orange.

The ratio in the solution of the carbon from steel is one to 1.38, or a slightly yellower orange; the ratio in the caramel is one to 1.42, while in the platinum cobalt it is one to 1.6, or a decidedly yellow orange.

It will be evident therefore, why an optical instrument of precision which promised to furnish a universal standard applicable anywhere, was eagerly welcomed.

The tintometer devised by Joseph W, Lovibond, of Salisbury, England, was examined by Dr. T. M. Drown in the inventors laboratory, and an instrument was imported for the use of the State Board of Health.

It consists of two tubes side by side with openings at one end and divided by a central taper partition terminating with a knife edge at the eye piece, which it divides equally in such a way that on looking through the eye piece the two openings are simultaneously visible. The liquid is placed in cells of definite lengths, one inch, two inches, up to twenty-four inches. The standards consist of three sets of graded colored glasses, red, yellow and blue, numbered according to their depth of color.

"By using several superimposed glasses from a set, a depth of color is represented by the aggregate of tint number on the glasses used, whilst glasses from different sets produce a composite color, and the exact proportion of each component color can be read off."

The use of the Lovibond instrument in our hands has been confined first, to the determination of the color scale which has been in use for the past eight years in the laboratory for water analysis of the Institute of Technology, and by which the numbers found in the reports of the Mass. State Board of Health, in the tabulated result of 15,000 samples, have been obtained; and

secondly, to a color comparison of some other substances in order to find some standard by which a quantitative estimation of the carbon present may be made.

The natural water color standards are prepared by dilution of a highly colored surface water with distilled water. At certain points in the scale the dilution is such that when the colors are read in 50 cc. tubes they match Nesslerized ammonia (0.01 mg. ammonia per cc.) standards read in the same volume and depth (23.5 cm.). The points in the scale at which this matching is made are at 0.2, 0.5, 1.3, 1.8 and 2.0.

Above the color standard of 2.0 the scale is prepared by dilution of the highly colored water in such a manner as to have the quantity of color proportionate to the depth in which the reading is made. For example, a color of 4.0 is prepared so that when read in one-half the usual depth, (*i. e.*, 11.75 cm.) it matches a color of 2.0 read in the full depth (23.5 cm.).

From the color 0.00 (distilled water) up to 0.2, and for the intervals between the points matched against the Nesslerized ammonia standards, the gradation is made by the eye.

The standard colors to be measured by the tintometer were prepared in this way, and were read in four different lengths of cell. Colors from 0.00 in the scale to 0.3 inclusive, were read in a twenty-four inch cell, from 0.3 to 1.5 in a six inch cell, from 1.5 to 4.0 in a two-inch cell, and from 4.0 upwards in a one inch cell. This method permitted the readings for the "standard yellow glasses" to be kept within 4.0 of the tintometric scale. This is desirable for the reason that the eye is liable to be less sensitive in reading above 4.0 of the "yellow standard glasses" than below that limit.

The following condensed table (No. 1.) gives the readings of the laboratory standards. The measurements are tabulated for convenience in units of yellow, red and blue of the tintometric scale. It must be understood, however, that the color transmitted to the eye when red and yellow glasses alone are used, and when the number of units of yellow exceed those of the red, is orange mixed with yellow. If yellow and blue glasses are used together, the color transmitted is violet with a mixture of blue or yellow,

as the case may be, depending upon the preponderance of one or the other of those colors. A neutral tint unit is obtained by a combination of three equal color units. Therefore, if the three colors are used, black or a decrement of normal white light is obtained.

TABLE NO. 1.

READINGS OF THE TINTOMETER "STANDARD GLASSES" FOR YELLOW, RED AND BLUE, WITH DIFFERENT LENGTHS OF CELLS USED.

	Natural water standard color scale.	Yellow.	Red.	Blue.	Yellow.	Red.	Yellow.	Red.	Yellow.	Red.
Section 1. Color of water measured in a cell 24 inches in length.	0.00	0.40		1.00						
	0.05	0.90		0.20						
	0.10	1.20	0.10							
	0.15	1.90	0.32							
	0.20	2.40	0.84							
	0.30	3.50	1.05		0.80	0.30				
Section 2. Color of water measured in a cell 6 inches in length.	0.40				1.10	0.42				
	0.50				1.35	0.58				
	0.60				1.60	0.66				
	0.70				1.85	0.80				
	0.90				2.40	1.10				
	1.00				2.80	1.25				
	1.20				3.20	1.55				
	1.30				3.50	1.70				
	1.50				3.90	1.85	1.20	0.60		
Section 3. Color of water measured in a cell 2 inches in length.	1.80						1.35	0.70		
	2.00						1.50	0.80		
	2.50						1.95	1.00		
	3.00						2.50	1.20		
	4.00						3.20	1.60	1.60	0.80
Section 4. Color of water measured in a cell 1 inch in length.	5.00								1.95	1.00

If the color sensations were transmitted uniformly, then having obtained a reading in a given length of cell for a color of 0.2 a color of 0.6 would give three times as much yellow and three times as much red, and a color of 1.8 would give nine times as

much yellow and nine times as much red, but as a matter of fact the actual reading shows sixteen times as much yellow and eight and two-tenths times as much red.

The following table will show this more distinctly:

READING OF 0.2 COLOR IN TWENTY-FOUR INCH CELL = 2.40 YELLOW, 0.80 RED.

		Calculated readings.		Observed readings.	
		Yellow.	Red.	Yellow.	Red.
Color	0.6	7.20	2.40	7.60	2.40
"	1.0	11.00	4.00	15.53	3.65
"	1.8	22.80	7.20	38.49	6.60

Therefore, in the case of a higher color a shorter length of cell is used, so that the readings may be always made with lighter colored glasses.

The second table (No. 2) represents the differences for each tenth of color in the natural water standard scale, beginning with 0.00 and running to 5.0, as measured by the tintometer "standard glasses" for both yellow and red. In one column is shown the estimated difference for yellow and red, if the increase in any section were proportional to the numerical increase of the natural water standard scale. The basis for calculation is arbitrary for each section. (The section here is the division made by reading in the different lengths of cell.) The basis of calculation for the first section (twenty-four inch cell) is the color standard (0.1) which reads yellow 1.20, red 0.10. For the six inch cell the color 0.3 which reads yellow 0.80, red 0.30. For the two inch cell, the color 0.5 which reads yellow 1.20, red 0.60, and for the one inch cell, the color 4.0 which reads yellow 1.6, red 0.80. It will be seen that the estimated and observed differences agree quite well and indicate a regular increment of color as the scale ascends.

Considering the fact that we have had the instrument in our hands for a few months only and that we have been able to give to it only the odds and ends of time which a full daily routine left at our disposal, and therefore, that we cannot claim to have as yet perfectly trained eyes, the results are very encouraging, especially as in the case under consideration, we have to deal with a mixture of very impure colors.

TABLE NO. 2.

Differences in the Tintometric Readings of Red and Yellow for Each Tenth of Color in the Natural Water Standard Scale.

	Natural water standard color scale.	Yellow.		Red.		Estimated difference.
Sec. 1. Color of water measured in a twenty-four inch cell	0.00					
	0.10	0.80				Yellow = 1.20
	0.20	1.20		0.74		Red = 0.10
	0.30	1.10		0.21		
Sec. 2. Color of water measured in six inch cell.	0.40	0.30		0.12		
	0.50	0.25		0.16		
	0.60	0.25		0.08		
	0.70	0.25		0.14		
	0.80	0.275	0.55	0.15	.30	
	0.90	0.275		0.15		Yellow = 0.27
	1.00	0.30		0.15		Red = 0.10
	1.10	0.25	0.50	0.15	0.30	
	1.20	0.25		0.15		
	1.30	0.30		0.15		
	1.40	0.20	0.40	0.075	0.015	
	1.50	0.20		0.075		
Sec. 3. Color of water measured in a two inch cell.	1.60	0.05		0.033		
	1.70	0.05	0.15	0.033	0.010	
	1.80	0.05		0.033		
	1.90	0.075	0.15	0.05	0.10	
	2.00	0.075		0.05		
	2.10	0.09		0.04		Yellow = 0.08
	2.20	0.09		0.04		Red = 0.04
	2.30	0.09	0.45	0.04	0.20	
	2.40	0.09		0.04		
	2.50	0.09		0.04		
	2.60	0.11		0.04		
	2.70	0.11		0.04	0.20	
	2.80	0.11	0.55	0.04		
	2.90	0.11		0.04		
	3.00	0.11		0.04		
	3.10	0.07		0.04		
	3.20	0.07		0.04		
	3.30	0.07		0.04		
	3.40	0.07		0.04		
	3.50	0.07	0.70	0.04	0.40	
	3.60	0.07		0.04		
	3.70	0.07		0.04		
	3.80	0.07		0.04		
	3.90	0.07		0.04		
	4.00	0.07		0.04		
Sec. 4. Color of water measured in a one inch cell.	4.10	0.035		0.02		
	4.20	0.035		0.02		
	4.30	0.035		0.02		
	4.40	0.035		0.02		
	4.50	0.035	0.35	0.02	0.20	Yellow = 0.04
	4.60	0.035		0.02		Red = 0.02
	4.70	0.035		0.02		
	4.80	0.035		0.02		
	4.90	0.035		0.02		
	5.00	0.035		0.02		

Table No. 1 will at least serve as a rapid method for the standardizing of the stock bottles of natural waters, as the observer's eye becomes trained and more knowledge is obtained of the conditions which influence readings, a more perfect scale may be constructed.

The direct use of the instrument with the construction of a chart for each water, is evidently out of the question where, as in our laboratory, the color must be determined on twenty or thirty samples a day.

A modification of the tintometer has been proposed by H. R. Proctor, Yorkshire College, Leeds, England.[1]

This is designed to bring the color patches into juxtaposition as is done in the comparison of two spectra instead of having the separating dark band in the center. We have not been able to try this instrument, but it promises to be an improvement.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 15.]

ON THE ESTIMATION OF LEVULOSE IN HONEYS AND OTHER SUBSTANCES.

BY H. W. WILEY.

Received September 30, 1895.

A SIMPLE optical method for the estimation of levulose is of great advantage in the examination of honeys and other substances containing that body. The following optical method is one of easy application when the analyst has access to the jacketed observation tube, which will be mentioned below.

The principle of the process rests upon the change in the specific rotary power of levulose at different temperatures. The change in the optical rotation of other bodies associated with levulose in the condition of the experiments to be described is so little as to affect the data obtained to a very slight degree. The process, as it has been worked out, is easily applied and gives results which it is believed are better than those obtained by any other method.

The Observation Tube.—The most important adjunct of a mechanical nature in the process is an observation tube which

[1] *J. Chem. Soc. Ind.*, 14, 2, *1895*.

will permit of the polarimetric reading of a solution containing levulose at widely separated temperatures. The two temperatures adopted for experimental purposes are zero and 88°. The observation tube which was devised for the purpose is so constructed as to permit of its being surrounded entirely by a temperature control medium, either water or ice. Even the cover glasses of the tube devised are subjected to the temperature of the medium. The whole column of liquid under observation can in this way be brought to the same temperature, thus not only securing more accurate results, but removing the difficulties in the way of reading, produced by the refraction of light in passing through liquid media of different densities. The observation tube employed can be made either of glass or metal. The glass tube changes less in length on changing temperatures, but the metal tube is more sensitive and can be brought with its contents more quickly to a definite temperature. A tube, especially constructed for the purpose and made ot silver, is particularly convenient in the observation of solutions which have been inverted by the action of hydrochloric acid. When metal tubes are used the continuous kind is employed, permitting the displacement of one solution by another without the removal of the tube from its position. The length of the tube at ordinary temperature having been determined, correction is made for linear expansion or contraction at the temperature of observation. At low temperatures it is impossible to use an observation tube of ordinary construction on account of the deposition of moisture upon the cover glasses. This difficulty is entirely overcome by attaching to the ends of the observation tube, by means of a threaded screw, a tube made of hard rubber carrying a central axis of perforated brass of the same dimensions as the diameter of the observation tube outside of which are placed fragments of calcium chloride. The end of the tube is covered air-tight with an ordinary cover glass. Being screwed air-tight upon the observation tube, the calcium chloride at once absorbs all the moisture within the hard rubber cylinder and thus completely protects the cover glass from the deposition of water. Protected in this way the observation tube can be kept for hours at the temperature of zero, without any possibility of obscuring the

field of vision from deposited moisture. The construction of the protecting tube, together with the method of its attachments to the observation tube, is shown in the figure.

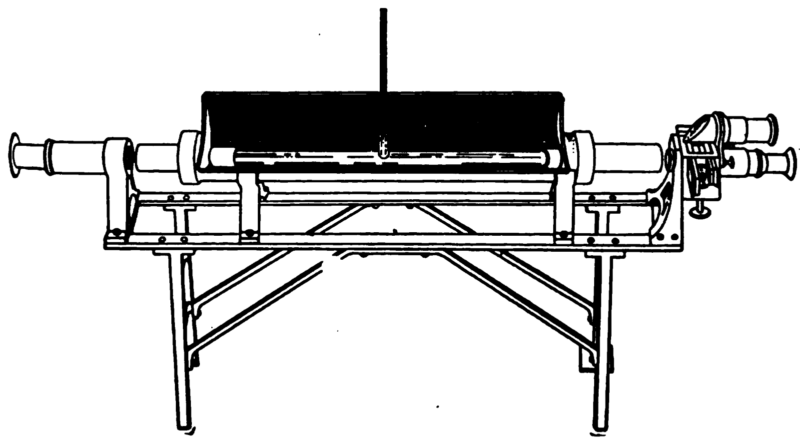


FIG. 1.—APPARATUS FOR POLARIZING LIQUIDS AT LOW TEMPERATURES.

For reading at low temperatures, especially at zero, the observation tube is held in a large metal receptacle coated on the outside with asbestos cloth and having a V-shaped slit above. A special stand is made for holding this apparatus to which is also fixed the optical parts of a double compensating Schmidt & Haensch half shadow polariscope. The construction of the stand and of the holder for the observation tube is shown in the figure, in which, however, the V-shaped slit is pushed down to one side in order that the photograph may show the position of the observation tube within. In practice the V-shaped slit is kept at the top and the observation tube is entirely surrounded by finely ground ice, an opening in the bottom permitting the water to escape as the ice melts.

The details of the construction of the observation tube are shown in a horizontal section through the center of the observation tube in Fig. 2. In this figure the observation tube, made of glass or metal, is represented by *i*, and the metal jacket, open at the top in the V shape as described, by *k*. The observation tube is closed by the heavy disk *b*, made of non-polarizing glass. This disk is pressed against the end of the observation tube by

the rubber washer *a* when the drying system about to be described is screwed on to *k*. The apparatus for keeping the cover glass dry is contained in the hard rubber tube *m*, and consists of a perforated cylinder of brass, *e*, supported at one end by the perforated metal disk *c* and at the outer end by the arm *d*. It is closed by a cover glass of non-polarizing glass *s* and can be screwed on to the system *h* at *n*. The space *p* is filled with coarse fragments of caustic soda, or potash, or calcium chloride by removing the cover glass *s*. The perforated disk *c* prevents any of the fragments from entering the axis of observation.

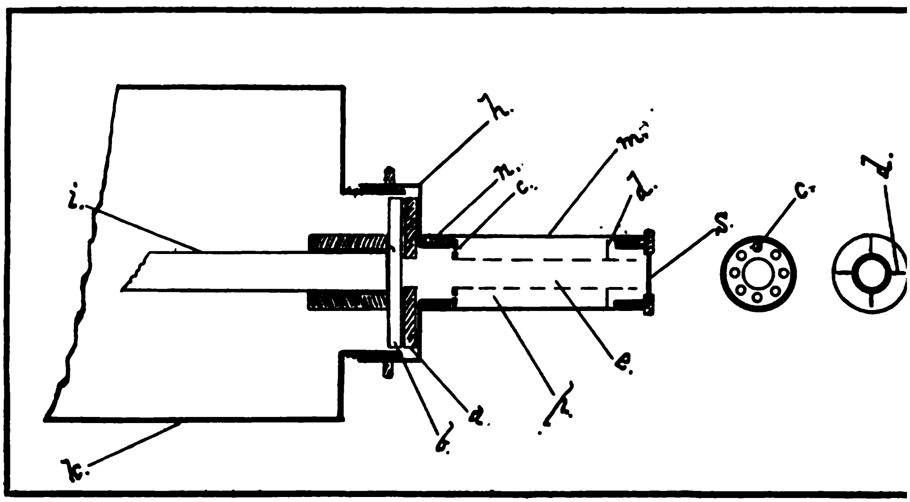


Fig. 2.—Details of Observation Tube.

When the cover glass *s* is replaced, it just touches the free end of the perforated metal tube preventing any of the fragments of the drying material from falling into the center at the outer end. When this drying tube is placed in position, the contents of the observation tube *i* can be kept at the temperatures of zero for an indefinite time, without the deposition of a particle of moisture either upon the glass *b* or *s*.

For observation at high temperatures, the apparatus described above may be used or it may be removed from the stand, which is so constructed as to receive a large box covered with as-

bestos felt an inch thick. The observation tube is held within this box in the same way as in the one just described so that the hot water extends not only the entire length of the tube but also covers the cover glasses. In both cases the cover glasses are made of heavier glass and are much larger in diameter than are the ordinary tubes for polariscopes. The protecting cylinders of hard rubber are not needed at high temperatures, but can be left on without detriment.

The illustration, Fig. 3, shows the arrangement of the apparatus with a silver tube, which can be filled and emptied without removing it, in position.

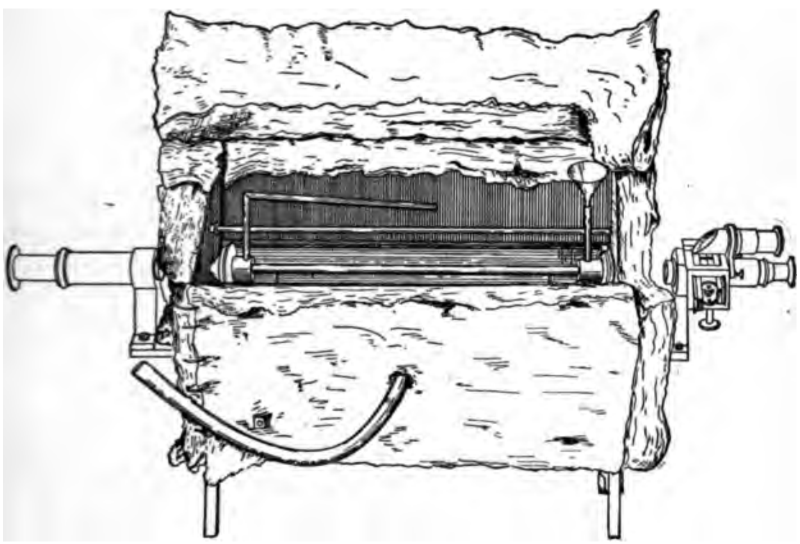


FIG. 3.—POLARISCOPE FOR LEVULOSE AT HIGH TEMPERATURES.

In practice the water is heated with a jet of steam and an even temperature is secured by a mechanical stirrer, kept slowly in motion. With such a box it is easy to keep a temperature for several hours which will not vary more than half a degree. The temperature for reading the hot solutions is fixed at 88°, this being the one at which a mixture of equal molecules of levulose and dextrose is optically inactive. In every case the sugar solutions are made up to the standard volume at the

temperatures at which they are to be read, and thus the variations due to expansion or contraction are avoided. When solutions are to be read at a high temperature, they must be made with freshly boiled water so as to avoid the evolution of air bubbles which may otherwise obscure the field of vision.

By means of the apparatus described it is easy for the analyst to make a polarimetric reading at any temperature desired. In all cases the observation tube should be left at least half an hour and sometimes longer, in contact with the temperature control medium before the reading is made. In the case of reading at zero it is also found that it requires several hours for a levulose solution containing other bodies, such as are found in honey, to reach a constant rotatory power. It is therefore necessary, in such cases, to leave the observation tube in contact with finely powdered ice for at least three hours before the reading is made. For ordinary analytical operations, however, this long delay is unnecessary.

The appearance of the field of vision is usually a pretty fair index of the point of time at which a constant temperature is established throughout all parts of the system. Any variation in temperature produces a distortion of the field of vision, while a constant fixed temperature will disclose the field of vision in its true shape and distinctness of outline.

The chief points of novelty in the apparatus described are, first, the immersion of the whole of the observation tube together with the cover glasses in the temperature medium used; and second, the protection of the external surfaces of the cover glasses from the deposition of moisture at low temperatures.

PRINCIPLES OF THE CALCULATION.

If 26.048 grams of pure sucrose be dissolved in water and the volume made up to 100 cc. it will produce an angular rotation of 34.68° when examined in a 200 mm. tube with polarized sodium monochromatic light. Upon the cane sugar scale of an accurately graduated Schmidt and Haensch shadow instrument the reading will be 100 divisions, corresponding to 100 per cent. of pure sucrose.

In the complete inversion of the cane sugar the reaction which takes place is represented by the following formula :

$$C_{12}H_{22}O_{11} + H_2O = \overset{-}{C_6H_{12}O_6} + \overset{+}{C_6H_{12}O_6}.$$

The minus and plus signs indicate that the resulting invert sugar is a mixture of equal parts of levulose (*l* fructose) and dextrose (*d* glucose). We are not concerned here with the fact that a complete inversion of cane sugar is a matter of great difficulty nor with the danger which is always experienced of destroying a part of one of the products of inversion. They are matters which may cause a variation in the analytical data afterward, but do not affect the principles on which the process is based.

In the inversion of 26.048 grams of cane sugar there are therefore produced 13.71 grams of levulose and 13.71 grams of dextrose, or in all 27.42 grams of the mixed sugars.

The angular rotation which would be produced with sodium light, by 13.71 grams of dextrose in a volume of 100 cc. and through a column 200 mm. in length is 14.55°, equivalent to 41.89 divisions of the cane sugar scale. The specific rotatory power of dextrose solution of the density given is almost exactly 53, and this number is used in the calculations.

In a mixture of the two sugars under the conditions mentioned and at a temperature of 0°, the angular rotation observed is —15.15° equivalent to 43.37 divisions of the cane sugar scale.

The + rotation due to the dextrose present is 14.53°. Therefore, the total negative rotation due to levulose at 0° is 15.15 + 14.53 = 29.68°. The specific rotatory power, therefore, of levulose at 0° and in the degree of concentration noted is readily calculated from the formula

$$-(\alpha)_D^0 = -\frac{29.68 \times 100}{2 \times 13.71} = 108.24.$$

Since at 88° the mixture of levulose and dextrose is neutral to polarized light, it follows that at that temperature the specific rotatory power of levulose is equal to that of dextrose, *viz.*: 53°.

$$-(\alpha)_D^{88^\circ} = -53^\circ.$$

The total variation in the specific rotatory power of levulose, between zero and 88°, is 108.24—53=55.24°. The variation for each degree of temperature, therefore, of the specific rotatory power of levulose is equal to 55.24 divided by 88, which is equal to 0.628°. From these data it is easy to calculate the specific rotatory power of levulose for any given temperature. For instance, let it be required to determine the specific rotatory power of levulose at a temperature of 20°. It will be found equal to $108.24 - 0.628 \times 20 = 95.68°$.

In these calculations the influence of the presence of hydrochloric acid upon the rotatory power of the levulose is neglected.

Since the variation in angular rotation in the mixture at different temperatues is due almost wholly to the change in this property of the levulose, it follows that the variation for each degree of temperature and each per cent. of levulose can be calculated. Careful experiments have shown that the variation in the rotatory power of levulose between 0° and 88° is represented by a straight line. For 13.71 grams per 100 cc. the variation for each degree of temperature is equal to $43.37 \div 88 = 0.49$ division on the cane sugar scale or $15.15 \div 88 = 0.1722°$ angular measure. If 13.71 grams of levulose in 100 cc. produce the deviations mentioned for each degree of temperature, one gram would give the deviation obtained by the following calculations:

For the cane sugar scale,

$$0.49 \div 13.71 = 0.0357°$$

And for angular rotation,

$$0.1722 \div 13.71 = 0.01256°.$$

The above data afford a simple formula for calculating the percentage of levulose present from the variation observed in polarizing a solution containing levulose, provided that the quantity of levulose present is approximately fourteen grams per 100 cc.

Suppose in a given case the difference of reading between a solution containing an unknown quantity of levulose at 0° and 88° is equal to thirty divisions of the cane sugar scale. What weight of levulose is present? We have already seen that one gram in 100 cc. produces a variation of 0.0357 division for 1°. For 88° this would amount to 3.1416 divisions. The total

weight of levulose present is therefore $30 \div 3.1416 = 9.549$ grams. In the case given 26.048 grams of honey were taken for the examination. The percentage of levulose was therefore $9.549 \div 26.048 = 36.66$ per cent.

If it be inconvenient to determine the polarimetric observations at temperatures so widely separated as 0° and 88° the interval may be made less. In the above case if the readings had been made at 20° and 70° the total variation would have been only 50/88 of the one given, *viz.*: 17.05 divisions of the cane sugar scale. The calculation would then have proceeded as follows:

$$0.0357 \times 50 = 1.785.$$

Then $17.05 \div 1.785 = 9.552$ grams of levulose, from which the actual percentage of levulose can be calculated as above.

For honeys the operation is to be conducted as follows:

Since honeys contain approximately twenty per cent. of water and in the dry substance have approximately forty-five per cent. of levulose, about 38.50 grams of the honey should be taken to get approximately 13.8 grams of levulose.

In the actual determination the calculations may be based on the factors above noted, but without respect to the degree of concentration. If only half the quantity of dextrose noted be present its specific rotatory power is only reduced to 52.75° and this will make but little difference in the results. In the case of honey only 13.024 grams of the sample are used in the examination, half the normal weight for the Ventzke sugar scale. The error however due to difference in concentration is quite compensated for by the ease of clarification and manipulation. Alumina cream alone is used in the clarification, thus avoiding the danger of disturbing the rotatory power of the solution due to the presence of an excess of lead acetate.

An interesting fact is observed in cooling solutions of honey to 0°. The maximum left-handed rotation is not reached as soon as the temperature reaches 0°, but only after it has been kept at that temperature for two or three hours. The line representing the changes in rotatory power, in solutions of honey between 0° and 88°, is practically straight but from 10° to 0°, if measured by the readings taken without delay, it is decidedly

curved ; the reading being less at first than it really is afterwards. After three hours the 0° becomes sensibly constant and then the whole line is nearly straight but still with a slight deficiency in the reading at the 0°. For this reason the computations should be based on readings between 0° and 88° rather than on a number covering the whole range of temperature. Nevertheless, if the solution be kept at 0° for three hours before the final reading is taken no error of any practical magnitude can be introduced.

The calculations given above for the cane sugar scale can also be made in an exactly similar manner for angular rotation. The angular variation produced by one gram of levulose for 1° of temperature is 0.01256°. For 88° this would become 1.10528°. Suppose the total observed angular deviation in a given case between 0° and 88° to be 10.404°. Then the weight of levulose present is 104.04 ÷ 1.10529 = 9.413 grams.

In the case mentioned 26.048 grams of honey were taken for the examination. The percentage of levulose present therefore was 0.413 ÷ 26.048 + 36.13.

GENERAL FORMULA FOR THE CALCULATION OF PERCENTAGE OF LEVULOSE.

Let K = deviation in divisions of cane sugar scale or in angular rotation produced by one gram of levulose for 1° temperature.

Let T and t' = temperatures at which observations are made.

Let R = observed deviation in rotation.

Let W = weight of levulose obtained.

Let L = per cent. of levulose required.

Then $$L = \frac{R}{K(T-t')} \div W.$$

In most genuine honeys the value of R between 0° and 88° is approximately thirty divisions of the cane sugar scale or 10° angular measure for 26.048 grams in 100 cc. read in a 200 mm. tube, or for 13.024 grams in 100 cc. read in a 400 mm. tube.

The method of analysis outlined above has been applied in the examination of a large number of honeys with most satisfactory results. It can also be applied with equal facility to other substances containing levulose.

NOTES ON A FEW PYRIDINE ALKYL IODIDES.[1]

BY ALBERT B. PRESCOTT.

Received November 27, 1895.

PYRIDINE METHYL IODIDE.[2]

Preparation.—Of rectified pyridine, boiling at 116°–118° C., fifteen cc. are taken in a flask immersed in cold water and carrying a reflux condenser, and twelve cc. methyl iodide added, in very small portions at first, when the reaction is violent Boiling is moderated by the rate of the addition. After standing half an hour, the resulting crystalline mass, light straw colored, is warmed on the water-bath without the condenser, and more methyl iodide very gradually added until, as a result, the odor of pyridine disappears. Any excess of methyl iodide is distilled off on the water-bath. The mass is now dissolved in sufficient warm absolute alcohol, from which it crystallizes on cooling, and the product recrystallized in the same way several times, until colorless crystals are obtained. Colorless crystals are sometimes obtained in the second crystallization. From alcohol of ninety to ninety-five per cent. strength the crystallization is much less satisfactory. The mother liquids, on the addition of ether, yield a considerable precipitate of the product, and this can be crystallized from absolute alcohol.

Properties.—The crystals are flat pencils, sometimes aggregated in rosettes. They are very soluble in water, soluble in alcohol, methyl alcohol, chloroform, acetone, and in glacial acetic acid; not soluble in ether, or benzene, or carbon disulphide. The crystals are very slowly deliquescent, to a degree scarcely affecting weight after several hours exposure to the air. The melting point is 117° C.

1 Read at the Springfield meeting of the American Association for the Advancement of Science, Aug. 30, 1895.

2 From the experimental work of Mr. P. T. Trowbridge. Anderson stated the additive reaction of pyridine with alkyl iodides in 1855. In making such an addition-product, as a means of distinguishing pyridine from its homologues in analysis, he took ethyl iodide, *Ann. Chem.* (Liebig), 94, 364. Hofmann resorted to pyridine in his study of the reaction of *dihalogen* substituted hydrocarbons with tertiary base, but not earlier, that I have been able to find.—*1861: Proc. Roy. Soc.*, 11, 261. O. Lange, in 1885, in the course of work on the formation of picolines by Ladenburg's method of transposition, gives some account of pyridine methiodide.—*Ber. d. chem. Ges.*, 18, 3436. O. de Coninck, in 1883, proposed the additive reactions with methyl iodide in contrast with those of ethyl iodide for distinction between pyridine derivatives and quinoline derivatives.—*Bull. Soc. Chim.* [2], 40, 276.

PYRIDINE ETHYL IODIDE.[1]

Preparation.—It has been directed to bring about the addition of ethyl iodide to pyridine by heating the mixture of the two in sealed tubes. Trial was made of three ways, (1) by heating in sealed tubes at 120° C.; (2) by heating in pressure flasks at 100° C.; (3) by occasionally shaking in a flask at the temperature of the room. The last stated method gives much the best results. The ethyl iodide should be taken in a slight excess of the chemical proportion, and added all at once. With considerable quantities the heat of chemical action after a short time needs to be moderated by cooling, to prevent vaporization of the materials. The action is usually complete within two hours, the contents of the flask becoming solid. The crystalline mass is dissolved in enough warm absolute alcohol, and crystallized, more perfectly by the low temperature of a freezing mixture, recrystallizing until white. Addition of ether to the absolute alcoholic solution causes crystalline precipitation, and in this way the mother liquids may be made to yield final portions. Like addition of chloroform precipitates an oily mass.

Properties.—The crystals are colorless plates, permanent or slightly deliquescent, soluble in water, alcohol, methyl alcohol, acetone, and glacial acetic acid, from which it crystallizes, and slightly soluble in ethyl acetate; insoluble in ether, benzene, carbon disulphide, and in chloroform. The melting point is 90.5° C.

PYRIDINE PROPYL IODIDE,[2] $C_5H_5N.CH_2CH_2CH_3I$.

Preparation.—Pyridine rectified to boil at 116.5°–118.5°, and normal propyl iodide distilling at 102° C., are taken in molecular proportions of the two, but with a slight excess of the iodide. The two are digested together under pressure in a sealed tube at 130° C., for an hour. On cooling the resulting yellowish mass is dissolved in warm absolute alcohol, from which plate-form crystals of the addition product separate on cooling. If

[1] From the experimental work of P. F. Trowbridge in this laboratory. T. Anderson, 1855: *Trans. Roy. Soc. Edinb.*, 21, (4) 571; *Ann. Chem.* (Liebig), 94, 364. O. de Conick, 1883; *Bull. Soc. Chim.* [2], 40, 276.

[2] From the experimental studies of Mr. S. H. Baer. In Ladenburg's account of the formation of propylpyridine hydriodide, by transposition of pyridine propyliodide (*Ber. d. Chem. Ges.*, 17, 772) no description of the last named body is given.

not white it is to be recrystallized from the same solvent. Addition of ether to the absolute alcohol solution throws it down in a crystalline precipitate. Like addition of chloroform separates it as an oil-like liquid. From alcohol of ninety-five per cent. it is precipitated as an oil by addition of ether. In analysis of the preparation, it gave for iodine 50.63 per cent. in comparison with 51.00 per cent. by calculation.

Properties.—In colorless plate-form crystals, deliquescent, soluble in water, alcohol, amyl alcohol, ethyl acetate, and in benzene; insoluble in ether and in chloroform. The melting-point is between 52° and 53° C.

PYRIDINE ISOPROPYL IODIDE,[1] $C_5H_5N.(CH_3)_2CHI$.

Preparation.—By the same method, and under the same conditions already given for the corresponding normal propyl compound, but using a greater excess of the alkyl iodide, namely about one and a half molecules of the isopropyl iodide (boiling at 89°–90° C.) to one molecule of pyridine. The product solidifies in a crystalline mass while in the sealed tube, more readily and completely than the product of normal propyl iodide and pyridine, and it crystallizes more readily from absolute alcohol. In analysis, the iodine found was 50.64 and 50.50 per cent. in comparison with 51.00 per cent. by calculation.

Properties.—Colorless crystals, soluble in water, alcohol of ninety-five per cent., and in ethyl acetate: less freely soluble in absolute alcohol, amyl alcohol, or chloroform; insoluble in ether. The melting point is 114°–115° C.

COMPARISON OF MELTING POINTS.

As set forth below the addition compounds of the one base pyridine with different alkyl iodides, $C_nH_{2n+1}I$ show a gradation of melting points, a gradation which appears among the homologous normal members of the series, and again appears between isomeric members. The solubilities of these addition compounds show a correspondence to their melting points, agreeing with the generalization of Carnelly.[2] Pyridine

[1] From the work of Mr. S. H. Baer in this laboratory. Schrader (Inaug. Diss. at Kiel, 1884) obtained this quaternary iodide, by treatment at 100° C., as a yellow-white crystalline mass, convertable to the corresponding chloride (Ladenburg's Handwörterbuch, 9, 464. Ladenburg and Schrader, *Ber. d. chem. Ges.*, 17, 1121.)

[2] *Phil. Mag.*, (5) 13, 180; *J. Chem. Soc.*, 53, 782.

combination has been resorted to for various characteristics distinctive of alcohol radicals, by de Coninck, as cited in the beginning of this paper, and by Lippert[1] in 1893. The iodides of these quaternary base give constants more distinctive of composition than to do the platinum chlorides, at least so far as melting points of the iodides are available. In tabulating the melting points of the pyridine alkyl iodides it appears that, comparing homologous and again comparing isomers, the melting points of the addition products *fall* as the boiling points of the free alkyl iodides *rise*.[2] The same reverse ratio appears among picoline alkyl iodides. On the contrary, comparing pyridine methyl iodide with picoline methyl iodide, the two tertiary bases being homologous and the alkyl iodides being the constant factor, it is found that the melting point of addition compound rises as the boiling point of the tertiary base rises, and in an extreme proportion.

QUATERNARY BASE IODIDES.

	Melting points.	Boiling points of the free alkyl iodides.
With homologous alkyls :		
Pyridine methyl iodide	117° [3]	45°
Pyaidine ethyl iodide	90.5° [3]	72°
Pyridine propyl iodide	52–53° [4]	102°
(Pyridine butyl iodide decomposes before melting[5]		130°)
a-Picoline methyl iodide	226.5–227° [6]	45°
a-Picoline ethyl iodide ; ......under......	100° [7]	72°
With isomeric alkyls :		
Pyridine isopropyl iodide.................	114–115° [4]	89°
Pyridine propyl iodide	52–53° [4]	102°

QUATERNARY BASE METALLIC CHLORIDES.

(Pyrivine tertiary butyl salts are not formed)[5]		100°
Pyridine isobutyl platinum chloride	220° [5]	119°
" " gold chloride	139° [5]	

[1] *Ann. Chem.*, (Liebig), 276, 182.

[2] This reverse ratio does not hold good between ethyl and isopropyl, in their pyridine iodo-products, the one being not the direct homologue, but the isomer of the homologue of the other. In 1882 Carnelly remarked of "isomeric compounds" as shown by many instances, that their melting points follow a rule the reverse of that accepted for their boiling points, namely that "those melt the highest in which there are the greatest number of side chains." (*Phil. Mag.* (2), 13, 126).

[3] Trowbridge. [4] Baer. [5] Lippert: *Ann. Chem.* (Liebig), 276, 182.

[6] Ramsay: *Phil. Mag.* (5), 4, 241. Before the constitution of picoline was established. It is not necessary here to distinguish between isomeric picolines.

[7] Anderson: *Ann. Chem.* (Liebig), 94, 361.

	Melting points.		Boiling points of the free alkyl iodides.
Pyridine secondary butyl platinum chloride	191°[1]		119°
" " gold chloride		129°[1]	
Pyridine normal butyl platinum chloride ..	205°[1]		130°
" " " gold chloride..........		111°[1]	

With homologous tertiary bases:		The free tertiary bases.
Pyridine methyl iodide....................	117°[2]	116°
Picoline methyl iodide	226.5–227°[3]	132–140°

Comparing two isomeric addition compounds:		Ter. base.	Alk. iod.
Pyridine ethyl iodide, $C_5H_5N.C_2H_5I = C_7H_{10}NI$	90.5°[2]	116°	72°
Picoline methyl iodide, $CH_3.C_5H_4N.CH_3I = C_7H_{10}NI$	227°[3]	132°	45°

In the comparison last above, there are two quaternary base iodides having the same empirical formula, and having near the same mean of boiling points of the uniting constituents, while the difference between their quoted melting points is something surprising. We should expect, however, from anology with the previous comparisons, to find a double homologous difference in this case. The transfer of the homologous CH_2, so to speak, *from* the alkyl of the compound *to* the amine of the other compound, should exert a two-fold effect in raising the melting point.

In a paper by Mr. Flintermann[4] and myself, some data are given in small part from our own work and more from the work of others, as to the limits of additive combination of isomeric alkyls with tertiary amines, especially with pyridine, in formation of quarternary bases. It would seem desirable to compare these apparent limits of additive formation with the generalizations of Carnelly and others upon the cohesion constants of isomers at large. Therewith these few facts of the melting points of pyridine quaternary bases are presented, though requir-

[1] Lippert: *Ann. Chem.* (Liebig), 276, 182.

[2] Trowbridge.

[3] Ramsay: *Phil. Mag.* (5), 4, 241. Before the constitution of picoline was established. It is not necessary here to distinguish between isomeric picolines.

[4] Dipyridene trimethylene dibromide, etc., this Journal, 18, 28.

ing more data, with the re-examination of figures of early data, as a part of the study of the chemical character of the nitrogen bases. To the same end some work upon the hydroxides of these bases is nearly ready for presentation from this laboratory. And to the same end work is being continued upon the periodides,[1] and other superhalides, that these extreme additive combinations may show something of the base-making power of nitrogen.

UNIVERSITY OF MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

AN ELECTROLYTIC METHOD FOR THE DETERMINATION OF MERCURY IN CINNABAR.

BY W. B. RISING AND VICTOR LENHER.

Received November 11, 1895.

WHEN a rapid solution of cinnabar is desired, heretofore, oxidation with aqua regia has seemed most convenient; the length of time required to expel the nitric acid used, and the likelihood of loss of mercury by distillation in hydrochloric acid, are serious hindrances to the use of this method. Hydrobromic acid dissolves very readily mercuric sulphide, as well as many other naturally occurring sulphides with the evolution of hydrogen sulphide and the formation of the bromide.

If this solution be nearly neutralized with caustic potash, pure potassium cyanide added in sufficient excess to dissolve the cyanide first precipitated (Smith, Electro-Chemical Analysis, p. 58), and electrolyzed with a weak current, the mercury will be readily deposited as metal on a platinum dish used as a negative electrode. The use of hydrobromic acid is to be recommended, as it gives such a ready method of decomposition, and can be used at low temperatures, when there will be no loss of mercury by distillation.

The hydrobromic acid used in the following experiments was prepared by treating potassium bromide with sulphuric acid of 56° Baumé; the gas was conducted into water, as in the preparation of hydrochloric acid. By using potassium bromide

[1] This Journal, 17, 775, 859.

with the above strength of acid, hydrobromic acid quite free from bromine, can be readily prepared.

The ordinary hydrobromic acid used in the laboratory, containing bromine, could be used in the following experiments:

The first sample which was worked with was pure mercuric sulphide. Hydrobromic acid of constant boiling point, *i. e.*, forty-nine per cent., was diluted with water one to four, and the sample treated with as little excess as possible over what would be necessary for its solution; the slight excess of acid was neutralized with potassium hydroxide, potassium cyanide added in excess and the solution electrolyzed by a current giving 0.025 amperes $N. D._{10}$

The following results were obtained:

Mercuric sulphide. Gram.	Mercuric found. Gram.	Mercury. Per cent.
0.2110	0.1818	86.16
0.2058	0.1774	86.20

The second sample was a naturally occurring cinnabar; determination (*a*) was made, using the decomposition by aqua regia, evaporating off the excess of nitric acid with hydrochloric, neutralizing the excess of hydrochloric acid with potassium hydroxide, adding potassium cyanide in excess and electrolyzing as before. (*b*) and (*c*) were treated with twenty per cent. hydrobromic acid at the boiling temperature; solution was effected in a few minutes, the excess of acid was neutralized by potassium hydroxide, potassium cyanide added in excess and electrolyzed with the same strength of current as before.

Results were:

	Cinnabar. Gram.	Mercury found. Gram.	Mercury. Per cent.
(*a*) ·······	0.2024	0.1046	51.68
(*b*) ·······	0.2514	0.1299	51.67
(*c*) ·······	0.5135	0.2656	51.72

The last sample was a lower grade cinnabar, very silicious, and long digestion with either hydrobromic acid or aqua regia was necessary. In this last experiment the action of the hydrobromic acid was very much more rapid than that with aqua regia. The mercury was deposited from a cyanide solution as before.

Results were, using hydrobromic acid as solvent:

	Cinnabar. gram.	Mercury found. gram.
(*a*)	0.2011	0.0616
(*b*)	0.2011	0.0622

Using aqua regia as solvent:

	gram.	gram.
(*a*)	0.2030	0.0629
(*b*)	0.2030	0.0631

NEW BOOKS.

THE SCIENTIFIC FOUNDATIONS OF ANALYTICAL CHEMISTRY TREATED IN AN ELEMENTARY MANNER. BY WILHELM OSTWALD. TRANSLATED BY GEORGE M'GOWAN. xviii, 207 pp. 8vo. London and New York: Macmillan & Co. Price, $1.60.

The little book before us undertakes, as its title indicates, a scientific presentation of the principles which underlie the physico-chemical phenomena upon which the art of analyses depends for the separation, detection and determination of the various substances with which it deals. In this undertaking the electrolytic dissociation theory is freely made use of and with such success that a flood of light is let in upon many of the obscurer phenomena encountered in the ordinary course of analysis.

The presentation of the subject is elementary in the best sense, but little in the way of previous knowledge being assumed, while by the clearness of statement and logical order of ideas preserved throughout, the author has fairly deserved the right to be named with the great masters of scientific style, with Tyndall and with Hofmann.

The theory and its applications are separately considered. Under the former head we find a discussion of the theory of the washing of precipitates and of the absorption phenomena which are of such importance in that process, further, of physical methods of separation, such as distillation, of the law of mass action, of supersaturation and of many other topics, the treatment of all being condensed and full of suggestions to the thoughtful reader.

In the special or applied part the analytical reactions of the metallic and acidic ions of the various analytical groups are taken up in detail, but briefly.

Lest it should be thought that this work is a piece of special pleading in behalf of the electrolytic dissociation theory, it is but just to the author to state that though written from the stand-point of that theory, the book is not *doctrinaire*, but is broad enough to be read with much interest by all chemists, whether they agree with the author's special views or not.

Much credit is due to Dr. M'Gowan for the smooth and scholarly translation now placed at the disposal of the English reading public, which annihilates the only excuse any English speaking chemist could offer for unfamiliarity with the most important work on the theory of analysis which has ever appeared. LAUNCELOT ANDREWS.

PRACTICAL PROOFS OF CHEMICAL LAWS. BY VAUGHAN CORNISH. New York: Longmans, Gre.,n & Co. Price 75 Cents.

This little work adopts a practical method for the explanation of "Dalton's Atomic Theory and the Laws of Combining Proportions." The first chapter is devoted to statements of these laws, and is followed by a chapter on the use of the balance. These prepare the student for the subsequent six chapters, which are devoted to the experimental part, in each case preceeded by a list of the necessary apparatus and followed by an example and an account of the original experiments, together with references to the original literature. The experiments are well chosen, calculated to give good results with simple and inexpensive reagents and apparatus. The arrangement is a time-saving one, and where time for laboratory work is very limited, as in higher schools, this fact will figure largely.

HERMANN FLECK.

ORGANIC CHEMISTRY. THE FATTY COMPOUNDS. BY R. LLOYD WHITELEY, F.I.C., F.C.S. New York: Longmans, Green & Co. 1895. 8vo. viii, 291 pp. Price, $1.00.

The publication of this manual, strinkingly similar in purpose, arrangement and matter to the "Organic Chemistry, Part I," of Perkin and Kipping, issued last year, shows that the needs of elementary students of this department of chemistry are now recognized more generally than they have been heretofore, and indicates, perhaps, that the number of chemists, who feel able to

supply their needs, is increasing. Whether this latest effort to make a satisfactory text-book is successful, can be determined only by giving the book a trial. Without unnecessary detail, the author has furnished a clear presentation of the main facts and theories pertaining to the "fatty compounds," giving also directions for the preparation in the laboratory of many compounds, and methods for their identification. These directions are generally clear and accurate.

The discussion of stereochemical theories is hardly full enough even for an elementary book, and the average student would probably find the chapters on the polyhydric alcohols and their derivatives more intelligible and interesting, if some of the methods recently employed for their synthesis and study, had been briefly explained. The book is attractively printed, and has a satisfactory index. L. B. HALL.

BOOKS RECEIVED.

How to Disinfect: A guide to practical disinfection in every-day life, and during cases of infectious illness. By C. T. Kingzett, F.I.C., F.C.S. New York: The American and Continental "Sanitas" Co., Ltd. Price ten cents.

Elements of Modern Chemistry. By Charles Adolphe Wurtz. Fifth American edition. Revised and enlarged by Wm. H. Greene, M.D., and Harry F. Keller, Ph. D. Philadelphia: J. B. Lippincott Co. 808 pp. Price $1.80.

Nineteenth Annual Report of the Connecticut Agricultural Experiment Station. Part II. Fertilizers. New Haven: Tuttle, Morehouse and Taylor Press. 74 pp. 1895.

Bulletin No. 58. Cutworms in Kentucky. Kentucky Agricultural Experiment Station. Lexington, Ky. 1895. 21 pp.

Bulletin No. 118. Cotttonseed Hulls and Meal for Beef Production. North Carolina Experiment Station. Raleigh, N. C., July 1895. 37 pp.

Bulletin No. 119. Volumetric Estimation of Phosphoric Acid. North Carolina Agricultural Experiment Station. Raleigh, N. C., August, 1895. 24 pp.

VOL. XVIII. [FEBRUARY, 1896.] No. 2.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 11.]

ACTION OF ACID AMIDES UPON BENZOIN.[1]

BY ALFRED NEWLIN SEAL.

Received November 29, 1895.

THE reactions of benzoin with a great number of bodies have been very extensively studied, but except the work of Anschütz and Gelderman[2] with urea and thiourea, no work has been done with the extensive class of acid amides. It was with the view of studying how these bodies would react with benzoin that this work was undertaken. It seemed very probable that by heating the amides with benzoin a condensation would be effected, as the hydrogen and the amido group of the former, as well as both the carbonyl and hydroxyl group of the latter, are very reactive. It was hoped in this way to prepare a series of condensation products from the amides of the homologous acids of the fatty and of the aromatic series. With this object in view, benzoin was heated in sealed tubes with various acid amides, in the presence of alcohol as a solvent, in varying proportions and under different conditions of time and of temperature.

Instead of finding the expected series of condensation products, however, it was discovered that with all the simple amides of both the mono- and dibasic acids of the fatty series, and with

[1] From the author's thesis presented to the University of Pennsylvania for the Degree of Ph.D., 1895.

[2] *Ann. Chem.* (Liebig), 261, 129.

two examples of the amides of the aromatic series, the reaction was preceded by the breaking down of the amide and the subsequent action of the ammonia on the benzoin, giving as the chief product of the reaction tetraphenylazine $C_4N_2(C_6H_5)_4$. The constitution of this body has been very carefully worked out by Japp and Wilson[1] and Japp and Burton.[2]

Not until after the action of several of the series had been tried with benzoin was the above conclusion reached, hence the following is a record of the reactions tried and of the results obtained. The work was carried out to a great extent in sealed tubes, the yields obtained were in many cases very small, the separation of the bodies produced difficult, and in some cases impossible, while the analyses were frequently extremely troublesome, as tetraphenylazine is remarkably stable and, as the experience of others has also shown, very difficult to analyze. As an instance of this, in one analysis, after six hours heating to redness with oxide of copper in a current of oxygen, graphitic carbon was found still remaining in the bottom of the boat. Later chromate of lead was used and the difficulties in great measure overcome.

I. GENERAL METHOD PURSUED IN STUDYING THE REACTIONS.

As the reactions of benzoin, with ten different amides, were studied, and the identification of the products proved more difficult than was anticipated, no attempt was made to induce condensation by means of dehydrating agents. In all the experiments, unless otherwise stated, benzoin and the amide, in definite, but varying proportions, were heated together with alcohol in sealed tubes. The amount of alcohol used at first was considerable, but the loss from explosions was so great that eventually the tubes were filled to but one-fifth or sixth of their capacity. When the tubes were opened there was generally a very considerable pressure. The presence of ammonia was very evident, and in many cases an ethereal odor was easily detected. Even if no ammoniacal odor could be detected, the alkaline reaction of the tube contents was always decided. Analyses of the gases obtained from the tubes showed from twenty-five per cent.

[1] *J. Chem. Soc.*, 49. 825.
[2] *Ibid*, 49, 843, and 51, 98.

to thirty-three per cent. of free ammonia. As the chief product of the reaction was identified as tetraphenylazine, and the accompanying bodies were those also produced by the action of ammonia on benzoin, there can be no doubt as to the interpretation of the result. Under the influence of the heat and alcohol the amide breaks down with the liberation of ammonia, and the formation of an ester with the alcohol. The ammonia then reacts with the benzoin, as has been already studied by Japp, Wilson and Burton.[1]

Japp and Wilson, in their study of the action of ammonia on benzoin, have reviewed the ground previously studied by Laurent[2] and by Erdmann[3] and found the products of the reactions to be tetraphenylazine $C_4N_2(C_6H_5)_4$, benzoinam $C_{28}H_{24}N_2O$, benzoinidam $C_{28}H_{23}NO_2$, and lophine $C_3N_2H(C_6H_5)_3$. In the study of the products of reaction with the amides, the presence of tetraphenylazine was proved in all cases, the presence of lophine in but one, benzamide, while another body was obtained which proved to be a mixture of the benzoinam and benzoinidam of Japp and Wilson.

The tetraphenylazine was identified by analysis, melting point, crystalline form, solubilities, color reaction with sulphuric acid, and also by a determination of the molecular weight. In the work, as given in detail later, some or all of these means of identification were used in each case. Lophine was identified by its melting point. It was only obtained with benzamide as the reacting body, and then only in very small amount. The apparent reason for its occurrence in this case will be discussed under the work with benzamide.

The other body obtained had, under various conditions, different melting points, and did not give concordant results when the different preparations were analyzed. Various methods of fractional crystallization and sublimation were tried to separate it into bodies of definite composition, but without success. With the exception of its solubility in alcohol, all its reactions indicated, as already stated, a mixture of benzoinam and benzoinidam.

[1] *Loc. cit.*
[2] *Jsb. phys. Wiss.*, 18, 354, and 26, 266.
[3] *Am. Chem.* (Liebig), 135, 181.

This action of the acid amides with benzoin, as essentially that of ammonia alone, is entirely in accord with the results obtained by Mason.[1] He found that oxamide and acetic acid heated together in sealed tubes at 220°–230°, reacted with the formation of acetamide.

II. ACTION OF THE AMIDES OF THE FATTY SERIES UPON BENZOIN.

a. Malonamide and Benzoin.—Malonamide and benzoin, in molecular proportions, were heated with alcohol on the water-bath in a flask connected with a return condenser for an hour. An examination of the material showed that no change had taken place, only benzoin and malonamide being found. The two bodies, in the same proportion, were then heated with alcohol in a sealed tube to 110° in a paraffine bath. As no change took place the tube was then heated at temperatures varying from 130° to 190°, with but little apparent change. The tube was then heated for eighteen hours at 200°. When opened a considerable pressure was evident and the odor of ammonia was very decided. The contents of the tube were poured out, and the crystals which had separated were filtered from the deep yellow liquid, pressed between filter-paper and treated several times with warm chloroform. Everything dissolved except a small amount of unchanged malonamide. The filtered solution was then evaporated nearly to dryness, the residue warmed with alcohol to remove coloring-matter, boiled four times with alcohol, and the insoluble portion dissolved in chloroform. From the first alcoholic filtrate on cooling crystals were obtained, melting, not at all sharply, at 190°–217°. The second filtrate gave white needles, melting at 192°–206°; the third filtrate crystals of the same form in less amount, melting at 193°–206°. The other two alcoholic filtrates yielded thicker needles in small quantity, melting at 243°–244°.

The three portions of crystals with the lower melting point were united and alternately treated with warm and boiling alcohol. By this means a series of products was obtained with all degrees of melting points between 193° and 220°. As the mate-

[1] *J. Chem. Soc.*, 55, 107.

rial is all easily soluble in chloroform and in benzoin, this gave no means of separation. An attempt at separation by means of sublimation was equally unsuccessful, the products showing the same wide range of melting point.

The three lots of crystals with high melting point and evidently much less soluble in alcohol than the other body were united, warmed with alcohol, and the residue dissolved in chloroform. On concentration of the solution large transparent crystals were obtained with a melting point of 245°.

The above method of separation and purification has been given in detail, as it was used with all the amides. Many portions of benzoin and malonamide were subjected to the above treatment, and the product with the melting point of 245° was proved to be tetraphenylazine by the results of the following examination:

	Substance.	H_2O	CO_2
I.	0.1351	0.0611	0.4384
II.	0.1416	0.0637	0.4585
III.	0.1339	0.0568	0.4343

IV. 0.2004 gram burned with copper oxide gave 13.8 cc. nitrogen at 26° and 764 mm.

	Calculated for Tetraphenylazine. $C_{28}H_{20}N_2$	Found. I.	II.	III.	IV.
Carbon	87.50	88.49	88.30	88.45	......
Hydrogen	5.21	5.02	4.99	4.71	......
Nitrogen	7.29	......	......	......	7.68

The melting point of tetraphenylazine as given by Japp and Wilson is 246°; the melting point as obtained for the body under consideration is 245° (uncorrected).

The molecular weight determination was made by the Raoult method, using benzene as the solvent. A Beckmann thermometer, graduated to 0.01°, was used, with the well-known Beckmann apparatus. The results were as follows:

$$L = 21.8262$$
$$C = 0.162$$
$$P\ 100 = 27.38$$
$$\text{Hence } CL = 3.5358$$
$$A = 0.1291$$
$$M = 379.5$$

Calculated for $C_{28}H_{20}N_2 = 384$

With concentrated sulphuric acid this body gives a beautiful red color, a very characteristic reaction for tetraphenylazine.

An analysis of the gas from one of the tubes in which the benzoin and malonamide had been heated, showed twenty-nine per cent. of ammonia.

b. Oxamide and Benzoin.—Oxamide and benzoin were heated together in molecular proportions at about 200°. The reaction at times took place with violent explosions and appeared to require a temperatere of 200°, as below this repeated attempts failed to produce any change. The bodies obtained were separated by the method already described. They were identical with those yielded by malonamide. One of them melted at 244°, gave a red color with concentrated sulphuric acid and crystallized from chloroform in prisms of the usual form. A molecular weight determination was as follows:

$$\begin{aligned} L &= 20.5973 \\ C &= 0.201 \\ P\ 100 &= 29.19 \\ \text{Hence } CL &= 4.1400 \\ A &= 0.1418 \\ M &= 345.6 \\ C_4N_2(C_6H_5)_4 &= 384 \end{aligned}$$

The other body gave an indefinite melting point from 193°–217°. Repeated crystallization failed to produce any body with a definite melting point.

I. 0.1073 gram burned with copper oxide gave 5.1 cc. nitrogen at 23° and 766.5 mm. = 5.39 per cent. nitrogen.

II. 0.1005 gram gave 4.9 cc. nitrogen at 25° and 763 mm. = 5.44 per cent. nitrogen.

Analyses of samples of gas from the tubes showed from twenty-five to thirty-three per cent. of free ammonia.

c. Succinamide and Benzoin.—Benzoin and succinamide were heated in molecular porportions at 200° for thirty-five hours. When the contents of the tube were treated in the usual way no unchanged succinamide remained, showing a complete decomposition. From the chloroform solution the same body separated in the usual crystalline form, melting at 245° and giving a deep red color with sulphuric acid. A molecular weight determination gave the following results:

$$\begin{aligned} L &= 17.9414 \\ C &= 0.175 \\ P\ 100 &= 27.73 \\ \text{Hence } CL &= 3.1397 \\ A &= 0.1381 \\ M &= 354+ \\ C_4N_2(C_6H_5)_4 &= 384 \end{aligned}$$

From the alcoholic filtrates white crystals were obtained melting from 192°–207°, with in one instance a small portion not melting until 216°. The analysis gave the following:

0.1033 gram burned with copper oxide gave 5.9 cc. nitrogen at 26.5° and 761 mm. = 6.32 per cent. nitrogen.

It will be noticed that this analysis shows a considerable difference from that of the similar body obtained from oxamide. This is another reason for supposing this body to be a mixture of benzoinam and benzoinidam. The former has the formula $C_{28}H_{24}N_2O$, giving 6.93 per cent. nitrogen and melting at "temperatures varying from 190°–220°, according as the temperature was raised slowly or rapidly." The latter has the formula $C_{28}H_{23}NO_2$, giving 3.45 per cent. nitrogen, and melting at 199°. That a mixture of these two bodies would give the results obtained as mentioned above, is natural. In the work of Japp and Wilson sufficient alcohol was put in the tubes to hold in solution much of the material produced, and hence the two bodies were separated. In the reactions, as carried out with the acid amides, the pressure of the evolved gases was so great that but little alcohol could be used. Hence only a small amount of the material produced was held in solution by the alcohol. This fully accounts for the non-separation of the two bodies by the method described by Japp and Wilson.

In order to compare the bodies obtained by the action of the amides upon benzoin with those obtained by the method as described by Japp and Wilson, benzoin was heated in sealed tubes with alcoholic ammonia. One tube was heated at 150°–180° for eight hours. The contents were then examined in the usual way and by means of the melting-point tetraphenylazine was found to have been formed, together with a body melting finally at 210°, but softening much below this. A second tube,

heated at 200° for several hours, also showed the formation of tetraphenylazine, but only very slight traces of any body melting at about 200°. But what was doubtless lophine was found in considerable amount, as shown by the isolation of a body melting at 272°. These reactions indicate that at higher temperatures lophine is produced, while at lower temperatures benzoinam is obtained in larger amount. This conclusion is strengthened by the observation that with only one amide was any lophine detected. This was with benzamide, which did not react with benzoin, except at temperatures much above those used with the other amides. It is true that the temperature at which the other amides react without producing lophine was equal to or even above that at which lophine was formed by the direct action of alcoholic ammonia. But this could be caused by the greater heat required for the breaking down of the amides. It seems quite possible that this might offer a means of studying the constitution of benzoinam.

d. Acetamide and Benzoin.—Benzoin and acetamide, in molecular proportions, heated together at 150° for four hours, did not react. Further heating at 190°–210° for six hours was also without effect. In a second tube the amount of acetamide was doubled and the tube heated for six hours at 150°, without any reaction taking place. In the next experiment four times the molecular quantity of acetamide was used for the benzoin employed, making about two grams of each and the tube was heated at 190°–210° for nearly six hours. When opened the odor of ethyl acetate was very evident, and an examination of the material showed that a reaction had taken place. Another tube with four grams of each was then heated at 190°–200° for six hours. When opened the odor proved both ethyl acetate and ammonia to be present. By means of repeated boilings with alcohol the usual bodies were separated and identified.

The tetraphenylazine melted at 242°, gave a deep red color with concentrated sulphuric acid, and crystallized from chloroform in the usual prismatic crystals. From the earlier alcoholic extracts bodies were obtained, melting at 192°–194° and 206°–209°. The yields were very small; but these observations would indicate that the reaction had taken place in the same manner as shown before.

e. Butyramide and Benzoin.—Butyramide was prepared by the method of Hofmann.[1]

In the first experiment 0.8 gram of the butyramide was heated with one gram of benzoin at 200° for six hours. No action took place. The tube was then heated for six hours at 250°; when opened the odor of ammonia was strong, and an ethereal odor was readily detected. A second tube, with double the above quantities of material, was then heated for eight hours at 200°, and for four hours at 220°. The contents of the two tubes were united and worked up as before with the usual results. The tetraphenylazine melted at 246°, gave an intense red color with sulphuric acid, and crystallized from chloroform in the usual prismatic form. The body soluble in alcohol melted at 193°–205°. In this instance the tetraphenylazine did not appear to be the principal product of reaction, as it was produced in much less amount than the lower melting body. This differs very decidedly from the usual reaction. The yields were small.

f. Valeramide and Benzoin.—In the first experiment with benzoin and valeramide one gram of each was used and the tube heated four hours at 200°. As no action had taken place it was then heated for several hours at temperatures varying from 230°–280°. When opened the usual combination of ammoniacal and ethereal odors was observed. Examinations of the small amount of product showed that a reaction had taken place.

To obtain more of the substance two more tubes, with larger amounts of material, were heated for several hours at from 220°–270°, until a change was evident. The contents of the three tubes were then worked up as before with the usual results. The yield obtained was very small, but tetraphenylazine was identified by the melting-point of 246°, the red color with sulphuric acid and the crystalline form. The other body melted at 193°–209°. As with butyramide, the relative proportion of the products was different from that observed with the amides of the dibasic acids, tetraphenylazine being produced in smaller amount than the other body.

III. ACTION OF THE AMIDES OF THE AROMATIC SERIES UPON BENZOIN.

a. Benzamide and Benzoin.—Molecular proportions of benzoin

[1] *Ber. d. chem. Ges.*, 15, 981.

and benzamide were first heated together in an oil-bath at 120°. No action took place. The tube was then heated at 150°–160°. Examination of the tube contents showed unchanged benzoin and benzamide and nothing else. A second tube, with the same amount of material (two grams of benzoin), was heated for six hours at 190°–200°, but without producing any reaction. Another tube, with double the amount of benzamide heated at 190°–200° for several hours, gave the same results, unchanged benzoin and benzamide being found, without anything else.

As these experiments had shown that benzamide would not react with benzoin under the same condition that the other amides did, further trials were made at higher temperatures, with better results. The first tube prepared with the amount of alcohol which had usually been used were all lost by explosion, at temperatures between 220 and 250°. The next tube prepared contained only a very small amount of alcohol with benzoin and benzamide in the molecular proportions of 1 to 2. It was first heated four hours at 250° without producing any change. A second heating for seven hours at 250°–260° was also without apparent action. Then for seven hours the tube was heated at 290°–300°, a portion of the time the temperature even rising to 360°. When the tube was opened there was no pressure apparent; the odor of ammonia was but slight, but the alkaline reaction of the liquid was strong. The yield of crystals obtained was very small, but melting point determinations showed that a change had taken place, with indications of the productions of tetraphenylazine and of some body with a higher melting point.

Another tube, prepared in the same way, was heated for seven hours at 250°–265°. As the crystals were deposited on cooling, the tube was opened and the contents examined. The yield was very small, but separation in the usual way, by means of boiling alcohol and chloroform, showed the formation of at least two bodies, which from their melting points indicated lophine and tetraphenylazine. There was no indication whatever of the presence of the bodies with melting points of about 200° and which were found as a part of the products of reaction of all the other amides with benzoin. As the only different condition

here was that of higher temperature, the same conclusion is reached that was pointed to with the experiments with alcoholic ammonia and benzoin; *i. e.*, the higher the temperature of reaction the less the amount of benzoinam and the greater the amount of lophine which is formed.

b. Salicylamide and Benzoin.—When heated together in the proportions of two molecules of salicylamide to one of benzoin, for six hours at 200°, the reaction was easily induced. When the tube was opened a slight pressure was evident, the liquid had a faintly alkaline reaction, but no odor of ammonia, while that of a salicylic ester was very noticeable. An examination of the crystals obtained from the tube was made in the usual way by means of treatment with boiling alcohol and chloroform.

Tetraphenylazine was found and identified by its melting point, color reaction with sulphuric acid and crystalline form. From the alcoholic extracts the usual body separated, with melting points varying from 192°–207°. Salicylamide therefore reacted just as the fatty amide did. About one-fifth of the original amide used was found unchanged in the liquid drained from the crystals in the tube.

In order to determine whether the amides would react with benzoin directly, without the intervention of a solvent, experiments were tried by heating them together in a dry condition.

When malonamide and benzoin were mixed together and heated by means of a paraffine bath at about 160°, action commenced and there was an evolution of gas, which proved to be ammonia. At 170°, the melting point of malonamide, the effervescence was very rapid. The heating was continued until the reaction had about ceased, and, on cooling, the reddish crystalline mass was boiled with alcohol and the residue dissolved in chloroform. The melting point determinations showed that tetraphenylazine had been produced, with slight traces of benzoinam.

Succinamide, when heated with benzoin in the same way, was also found to react with the evolution of ammonia. Benzamide, even when heated to 200° with benzoin, under the same conditions, was without action. These results are entirely in accord with those obtained in the presence of alcohol, and under pressure.

IV. THEORETICAL DEDUCTIONS.

Although in the nature of a repetition, the results of this work with amides may be summed up as follows:

Acid amides, heated with benzoin in alcoholic solution, do not yield condensation products in the true sense of the term, but break down with the liberation of ammonia and the formation of an ester with the alcohol. The ammonia then reacts with the benzoin in the way already studied by others.[1] This reaction takes place with the greatest ease with malonamide, and only with great difficulty and at high temperatures with benzamide. In every case tetraphenylazine is a constant product, while benzoinam and benzoinidam are produced at lower temperatures, lophine at higher. The presence of alcohol is not necessary to induce the breaking down of the amide, as the same results are obtained by the simple interaction of the dry materials. The great difference between the reactions of benzamide and of salicylamide is of interest as another example of the weakening of the benzene ring by the presence of hydroxyl in the nucleus of the latter.

V. A STUDY OF TETRAPHENYLAZINE.

a. Historical.—As tetraphenylazine was found to be the chief product of the action of amides upon benzoin, a further study of this body was instituted.

A brief review of what has been done in its preparation and investigation may be of interest. Laurent studied[2] the action of ammonia on benzoin. Later Erdmann[3] took up the same study and gave the name benzoinimide to what has since been shown to be tetraphenylazine by Japp, Wilson[4] and Burton. The very interesting work of these later investigators showed that, on distillation with lime, the so-called benzoinimide of Erdmann was converted into diphenanthyleneazotide, as it was then called. Ammonia acting on β-naphthoquinone was shown to produce $\alpha\beta$-naphthazine, a body whose constitution had been already proved through its syntheses by Witt[5] by the condensa-

[1] *Loc. cit.*
[2] *Ann. Chem.* (Liebig), 66, 181, and *Jsb. phys. Wiss.*, 18, 354, and 26, 666.
[3] *Ann. Chem.* (Liebig), 135, 181.
[4] *J. Chem. Soc.*, 49, 825 and 843, and 51, 98.
[5] *Ber. d. Chem. Ges.*, 19, 2794.

tion of β-naphthoquinone with $\alpha\beta$-diamidonaphthalene. As ammonia acting on phenanthraquinone yields the "diphenanthyleneazotide" this was also considered an azine, tetraphenyleneazine, and hence the so-called ditolaneazotide, which by distillation with lime yields the tetraphenyleneazine, was itself given the proper name tetraphenylazine.

Braun and Meyer[1] have produced this same body by the action of sodium amalgam on benziloxime, and have called it tetraphenylaldine. The only substitution product of tetraphenylazine which has been obtained is the tetra-nitro derivative prepared by Braun and Meyer. Attempts were, therefore, made to obtain bromine and chlorine derivatives, but, as the results will show, without success.

To obtain the material for study, the tetraphenylazine was prepared by the method described by Japp and Wilson, by heating benzoin with ammonium acetate in an open flask, and separating the azine from the other products of the reaction by means of alcoholic hydrochloric acid. This was found to be an entirely satisfactory method and gave a good yield of pure material, melting at 245°.

b. Bromination.—The azine was first heated with carbon bisulphide and an excess of bromine for eleven hours on the water-bath with return condenser. Acid vapors were given off in slight amount. An examination of the material showed that no bromination had taken place, the azine being found unchanged, melting at 245°. A second experiment was made by boiling a solution of the azine in strong alcoholic hydrochloric acid with bromine. An examination of the material showed that the azine was unaffected.

In the third experiment, chloroform was used as the solvent and bromine was added in the calculated quantity to produce a tetra-brom substitution product. Acid vapors were given off and the separation of dark red crystals appeared to indicate that a substitution had taken place. These, on exposure to air, rapidly lost their color, and by treatment with alcohol yielded the unchanged azine, as shown by the melting point and the absence of any halogen. Some of the reactions, as the action

[1] *Ber. d. chem. Ges.*, 21, 1269.

toward solvents, seemed to indicate that an unstable addition product might have been formed, but it is more probable that the red crystals represented simply a mechanical mixture of bromine with the azine. A repetition of the above, with the addition of a few crystals of iodine, gave the same results.

In the next trial some of the azine was heated in a sealed tube with bromine, a crystal of iodine and alcohol for seven hours at 200°–220°. When the contents were examined it was found that ethyl bromide and acetic acid had been formed, but that the azine was not brominated. The ethyl bromide was identified by its boiling point (38°–40°) and odor, and the acetic acid by its boiling point (115°–123°), and the formation of acetic ether with alcohol and sulphuric acid. The dark residue, when extracted with chloroform, gave the unchanged azine, melting at 244°. The insoluble black residue appeared to be carbon, not melting at 300°, insoluble in acids, alkalies or the usual solvents, burning with glowing, and not containing any halogen.

c. Chlorination.—Tetraphenylazine was dissolved in chloroform, and through the solution contained in a retort placed on the water-bath and connected with a return condenser, a stream of dry chlorine gas was passed for six hours. An examination of the material showed that no change had taken place. The same material was then subjected to the action of chlorine again, for the same length of time, with the same result. Aluminum chloride was then added to the contents of the retort and a rapid stream of chlorine was passed through for six hours, for a part of this time the retort being in direct sunlight. The residue, after removal of the solvent, was boiled with water, well washed, dried, and dissolved in chloroform. An examination of the material showed that no halogen had entered the body. Hence neither bromine nor chlorine substitution products could be obtained by the action of the halogens on tetraphenylazine. This great stability of the phenyl groups in the azine ring is of interest, and entirely in accord with analogy.

d. Nitration and Amidation.—Following the method employed by Braun and Meyer[1], the tetranitro derivative of tetraphenylazine was prepared by slowly adding the azine to cold, fuming

[1] *Loc. cit.*

nitric acid, with stirring. The deep yellow liquid was then poured into an excess of cold water, and the resulting voluminous light yellow powder filtered out, washed, and dried. It has an indefinite melting point between 140° and 150°. With concentrated sulphuric acid it gives an orange yellow color, very different from the brilliant red yielded by the unchanged azine.

To prepare the amido derivatives, the tetranitroazine was reduced with tin and hydrochloric acid. The clear red solution was diluted with water and the tin removed with hydrogen sulphide. The removal of the last portions of tin was extremely difficult, as not until repeated treatment with the hydrogen sulphide in a nearly neutral boiling solution could a base be obtained free from ash. When the filtrate from the sulphide of tin was made alkaline with ammonia an abundant yellow precipitate was obtained. During the filtration a portion of this appeared to undergo oxidation, as the precipitate, at first yellow, became green on the surface, and the filtrate, at first clear, became turbid on standing. The well-washed precipitate finally ceased to give a turbid filtrate and dissolved in hydrochloric acid with red color. Hydrogen sulphide, when passed into this solution, gave no precipitate. The solution was boiled, to remove the hydrogen sulphide, and made alkaline with ammonia, when a yellow precipitate was thrown down, which when filtered and washed, showed no change of color and gave a clear filtrate. When dried this base is of a brownish yellow color, is slightly soluble in chloroform, more readily in boiling alcohol. From the latter solution, on evaporation, it is obtained as before, in an amorphous condition without any sign of crystallization. When heated it darkens and melts above 260°, with decomposition and a slight sublimation.

To determine its composition, the hydrochloride was prepared by dissolving some of the base in dilute hydrochloric acid and evaporating the solution over sulphuric acid in a vacuum desiccator. No crystals could be obtained, but the material dried to a reddish-brown, transparent mass. It melts at about 140°, and is readily soluble in water. When the material, which had been dried over sulphuric acid, was heated to 100° in the air-bath, its

loss in weight would indicate five molecules of water of crystallization.

0.2867 gram, after heating at 100°, weighed 0.2480 gram = 13.49 per cent. water.

$$C_4N_2(C_6H_4NH_2HCl)_4 + 5H_2O = 13.23 \text{ per cent. water.}$$

0.2480 gram hydrochloride, dried at 100°, gave 0.2242 gram AgCl.

Calculated for $C_4N_2(C_6H_4NH_2HCl)_4$.	Found.
24.06 per cent. chlorine.	22.33 per cent. chlorine.

Platinic chloride, added to the aqueous solution of the hydrochloride, precipitates on standing a reddish-brown double salt.

0.1090 gram platinum double salt gave 0.0325 gram platinum = 29.81 per cent. platinum.

This corresponds to a salt of the composition:

$$(C_4N_2(C_6H_4NH_2HCl)_4)PtCl_4 + 11H_2O = 30.01 \text{ per cent. platinum.}$$

The filtrate mentioned before as obtained from the precipitation of the base by ammonia becomes turbid on standing and slowly precipitates a dark greenish-blue material. When acidified with hydrochloric acid it gives a dark green solution, which, under certain conditions of dilution, gives a deep blue color. This, when treated with hydrogen sulphide or zinc and hydrochloric acid, changes to green and finally to a yellow color. Standing exposed to the air, it gradually reverts to the blue color, while heating with nitric acid quickly produces the same change.

All these reactions indicate the presence of another base, possibly of two others of different composition. Their constitution was not further investigated.

e. Crystallographic and Optical Investigation.—As tetraphenylazine crystallizes from chloroform in brilliant prismatic crystals, an examination of the crystallographic and optical constants was made with the following results:

SYSTEM TRICLINIC.

$\breve{a} : \bar{b} : \acute{c} = 0.941^\circ : 1 : 0.5611.$

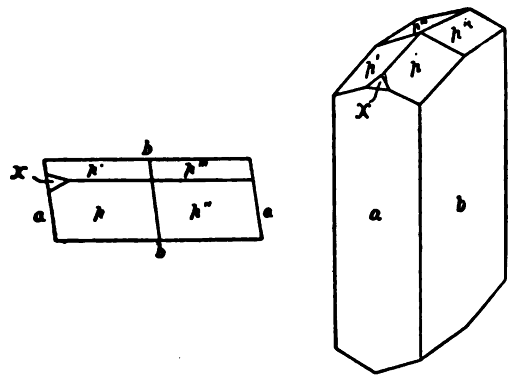
$\alpha = 83^\circ 48'$ $\beta = 85^\circ 13'$ $\gamma = 101^\circ 38'.$

$100 \wedge 010 = 101^\circ 13'$ ${}^1P \wedge 010 = 72^\circ 36'.$

Calculated $001 \wedge 010 = 86^\circ 20'$ $001 \wedge 100 = 84^\circ 36'.$

FORMS.

a (100 i—ī)	p (111 P')	p_2 (11ī 'P)
b (010 i—ĭ)	p_1(1ī1 'P)	p_3 (1īī P')
x (405 $\frac{4}{5}$—ī)		



OBSERVED ANGLES.

ab = 101°13′	b_1p^1 = 80°4′	$p_{//}p_{///}$ = 26°35′
bp = 72°36′	ap = 68°47′	$p_{///}p$ = 35°33′
$bp_{//}$ = 79°23′	ap_1 = 73°12′	$p_{/}p$ = 26°30′
b_1p_3 = 73°16′	pp_2 = 35°2′	ax = 55°42′

Crystals flat, tabular parallel to 010.

Cleavage none.

Optically negative, as determined by a quarter undulation mica plate.

Plane of optic axes parallel to ċ.

Apparent axial angle 2E = 18°.

EXTINCTION ANGLES.

On b........................parallel to edge ab.
On a........................parallel to edge ab.
On section normal to ċ = 14° with b.

Indices of refraction determined by the microscope method, using sodium light.

On b with edge ab normal to principal section of Nicol = 1.873
" " " " parallel " " " = 2.217
" " " " normal " " " = 1.946
" " " " parallel " " " = 1.897

VI. ACTION OF BENZOIN UPON UREA AND THIOUREA.

While studying the action of amides with benzoin, the reac-

tions with urea and thiourea were examined. Not until after considerable work had been done was it found that Anschütz and Gelderman[1] had previously studied these reactions and published their conclusions. The results that were obtained fully corroborated those of these chemists, and so will not be given in detail.

a. Urea and Benzoin.—Urea and benzoin, when heated together with alcohol in sealed tubes at 175°–195°, do not react as the true amides do, but form condensation products, with the elimination of water. That they react in this manner is to be accounted for by the fact that the two amido groups are both linked to the same carbon atom. It would be interesting to see whether the amides of the amido acids of the fatty and aromatic series would undergo condensations of the same nature.

The body obtained by the condensation of urea and benzoin dissolves in boiling alcohol, with a beautiful blue fluorescence and crystallizes in prismatic forms, which are dichroic. In the earlier work on these substances, it was found that under certain conditions this body is dimorphous, coming out from solution in two entirely distinct forms, one prismatic, as just mentioned, and the other in bunches of very delicate white needles. When the two forms were very carefully mechanically separated and dissolved in boiling alcohol, each solution, on cooling, showed crystals of both forms. The tendency was toward the assumption of the prismatic form. All attempts at ascertaining the conditions under which these could be produced were fruitless. Later work failed to give the needle form, only the prisms being obtained. That the two bodies were identical was shown by the melting points and determination of the nitrogen content. Both softened at about 280° and melted, not sharply, at about 318°. Analyses gave the following results:

NEEDLE FORM.

0.1023 gram substance, burned with copper oxide, gave 11.4 cc. nitrogen at 23° and 763 mm. = 12.59 per cent. nitrogen.

PRISMATIC FORM.

0.2022 gram gave 23.5 cc. nitrogen at 23° and 759.5 mm. = 12.70 per cent. nitrogen.

[1] *Loc. cit.*

The two bodies are therefore identical.

Extended study by Anschütz, Gelderman, and Schwickerath[1] has shown this body to be diphenylacetylenurein.

$$\begin{array}{l} C_6H_5\text{—}C\text{—}NH \\ \quad\quad\;\; \| \quad\quad\;\; \rangle CO. \\ C_6H_5\text{—}C\text{—}NH \end{array}$$

Analysis of the prismatic crystals mentioned above confirm this.

0.2203 gram substance gave 0.1044 gram water, and 0.6123 gram carbon dioxide.

	Calculated for $C_{15}H_{12}N_2O$.	Found.
Carbon	76.27	75.77
Hydrogen	5.09	5.26
Nitrogen	11.86	12.70
Oxygen	6.78	

Evans[2] has shown that condensations of urea with β-diketones can be induced by the influence of acids on their alcohol solution. Similar experiments were therefore tried with urea and benzoin. Urea was added to a saturated alcoholic solution of benzoin, and different amounts of concentrated hydrochloric acid added. No condensation was, however, produced.

b. Thiourea and Benzoin.—The thiourea used was prepared from ammonium thiocyanate. When heated with benzoin a condensation takes place, with the formation of what Anschütz and Schwickerath have shown to be $\alpha\beta$-diphenylglyoxaline sulphydrate. In the experiments with this body the two forms of crystals, as mentioned under the urea derivative, were produced, but the prismatic form was in very much the greater quantity, the needle form being only observed in very small amount. An attempt at producing the needle from in larger amount was made by using, instead of thiourea alone, a mixture of equal parts of this and ammonium thiocyanate. The results, however, were the same, only traces of the needle form appearing. This confirms the work of Anschütz, who found that the same body was produced whether thiourea or ammonium thiocyanate was used.

1 *Loc. cit.*, and *Ann. Chem.* (Liebig), 284, 8.

2 *J. prakt. Chem.*, 48, 489.

ON THE INVERSION OF SUGAR BY SALTS.

BY J. H. LONG.

Received December 5, 1895.

IT is a well known fact that the specific rotation of solutions of cane sugar is decreased by the presence of many neutral salts, even by sodium chloride and other salts of the alkali and earth groups. The amount of this decrease has been measured by several chemists, and recently very carefully by K. Farnsteiner,[1] who has noted the connection between the molecular weights of the salts dissolved with the sugar and the amount of the depression they produced. In a solution containing for each part of sugar three parts of water and 1.0036 parts of sodium chloride the specific rotation dropped from 66.6° to 62.47°. Similar effects were observed in other cases.

The extent of this depression is dependent to some degree on the temperature, but a temporary increase in temperature does not permanently alter the rotation. In illustration, a solution of pure saccharose containing in 100 cc. twenty-five grams of the sugar and ten grams of potassium nitrate gave a specific rotation of $\alpha^D = 66.22°$ at 20°. After heating one hour, but so as to avoid evaporation or pressure, the rotation was again determined and found to be practically the same. The solution was heated in a small flask closed with a perforated rubber stopper having a capillary glass tube in the perforation. It was possible by this means to heat the liquid to 100° in boiling water without risk of appreciable loss by evaporation.

On the other hand, a solution of sugar and zinc sulphate which gave a specific rotation of 64.98° when fresh, showed, after having been heated forty-five minutes in boiling water, as before, a specific rotation of 36.84°. In this case a decided inversion had taken place, as easily shown by other tests. The behavior of zinc sulphate is similar to that of a large number of other substances. Loewenthal and Lenssen[2] state that zinc sulphate and other neutral salts are without inverting action, but Béchamp, a little later[3] gave a list of these salts which are able to produce a marked inversion. The phenomenon is an inter-

1 *Ber. d. chem. Ges.*, **23**, 3570.

2 *Jsb. Chem.*, *1863*, 120, and Ostwald, Allg. Chemie, 2, 811.

3 *Jsb. Chem.*, *1864*, 573, and Gmelin, Handbuch der Org. Chem., iv., 1, 691.

esting one, and one which can now be easily explained, but until quite recently the literature has been almost silent on the subject. I wish to present in what follows a few observations bearing on the question.

Over a year ago in giving instruction to a class of students in the use of the polarimeter I suggested, as an illustration of a substance for examination, not free from color, the syrup of ferrous iodide of the pharmacopeia. Instead of exhibiting a more or less marked right hand rotation, as was expected, it was found to be strongly levo-rotary. The syrup, however, was known to be old and had been exposed to the light. As a certain practical interest attaches to the question it was decided to investigate fresh solutions.

The syrup of the pharmacopeia is made to contain in 100 cc. about 63 grams of sugar and 13.4 grams of ferrous iodide. On January 19, 1895, a liter of this solution was made according to the usual process, special care, however, being taken in the selection of the sugar and iodine employed. The liquid polorized immediately, in a 200 mm. tube, gave $\alpha_D = 81.15°$ at 20°. Four days later the rotation was found practically unchanged, the syrup having been kept meanwhile in the dark. A bottle holding about 100 cc. and furnished with a glass stopper was then filled with the syrup and allowed to stand until May 6th and exposed to diffused light. This portion now showed on polarization $\alpha_D = 53.12°$ in the 200 mm. tube, while the original, kept in the dark, polarized 63.17°. On this date, May 6th, a second portion of the original was filled into a botttle and allowed to stand in the light. It was polarized at different intervals, with results as follows, at 20°, in the 100 mm, tube:

July 15th	α_D	+6.66°
Aug. 25th	"	— 3.36°
Oct. 22d	"	—13.10°
Nov. 15th	"	—13.42°

Another portion of the orginal which had stood since January 19th in a small full bottle in the light gave now in the 100 mm. tube $\alpha_D = —15.66°$. From this it appears that in the interval the saccharose had undergone complete inversion. The original rotation observed, 81.15°, was that of a solution in which some inversion had already taken place.

Another solution was prepared on May 9th, containing in 250 cc. 140 grams of sugar and an amount of ferrous iodide corresponding to twenty-eight grams of iodine. The syrup and iodide solution were hot when mixed. This polarized at 20° gave a rotation of 33.25° in the 100 mm. tube, which corresponds to a specific rotation of 59.38°. At intevals the following rotations were found from two portions of this solution, which had been poured into glass stoppered bottles and kept in the light. One bottle was full and the other not quite full.

		Full bottle.	Partly filled.
July 13th	α_D	18.66°	+9.30°
Aug. 24th	"	8.58°	+3 56°
Oct. 22nd	"	3.76°	—10.16°
Nov. 15th	"	2.70°	—10.75°

It is apparent from the above that the presence of air in the bottle with the solution has a marked influence on the rapidity of inversion.

INFLUENCE OF TEMPERATURE.

The solution just described stood at the laboratory temperature during the time of the observations. A marked decrease in the time required for full inversion would naturally be expected by working at a higher temperature. This was shown by heating some of the last solution in boiling water during ninety minutes. The solution was contained in a flask with a capillary stopper. Before heating it had a rotation of 33.25° in the 100 mm. tube; after the application of heat the reading was —12.75° in the same tube. The following day the solution was reheated through three hours and polarized again, giving now —13.00° at 20°. Heating through ninety minutes was therefore sufficient to complete the reaction, and it is evident that an inversion which at the mean laboratory temperature of 20°–25° requires months for its completion may be accomplished in less than two hours at the temperature of boiling water.

It was found later that a moderate increase of temperature does not greatly hasten the inversion; this becomes rapid only above 60°.

INFLUENCE OF LIGHT.

It should be remarked thai the inversion by heat, as well as

by long standing in the light, is accompanied by a decided loss of color. A solution of ferrous iodide exposed to the air, or protected from the air and kept in the dark, soon becomes brown from partial decomposition aud separation of iodine, which is easily shown by the starch reaction. In stoppered bottles in the light, however, this decomposition is almost wholly prevented and in an already colored solution in which free iodine is shown by tests, the color is lost by exposure to the light.

Well-made undecomposed solutions of ferrous iodide are described as light green, but they may become almost as colorless as water, leaving the iron in a perfectly reduced condition. It has been found by numerous trials that the rate of inversion is more rapid in bottles exposed to the light than in similarly filled bottles kept in the dark. The rapidity of inversion is further increased if the solution is exposed to the action of light and heat together. More will be said of this later.

The phenomena described above are not confined to ferrous iodide but are exhibited by many other salts. In fact, from theoretical considerations, they should be expected in some degree from the salts of all the so-called heavy metals, as will presently be pointed out. First, however, some actual experimental results will be given.

FERROUS CHLORIDE.

A solution containing, in 100 cc., 50 grams of cane sugar and four and one-tenth grams of pure ferrous chloride was prepared. The ferrous salt was made by the action of an excess of iron on hydrochloric acid, and the syrup made with this and the sugar was bright green. It showed a rotation of 32.75° in the 100 mm. tube, or a specific rotation of 65.50°. After heating one hour to 100° the rotation was found to be —6.42° in the same tube.

FERROUS BROMIDE.

The solution contained in 100 cc., 50 grams of saccharose and ten grams of the bromide. The latter was made by the action of bromide and water on iron, and the solution so obtained was filtered into the dissolved sugar. The rotation of the fresh mixture was found to be 32.25°. A portion was heated one hour to 100° and was then polarized, after cooling to 20°, giving now a rotation of —10.26°.

FERROUS SULPHATE.

The solution of 100 cc. was made with fifty grams of sugar and ten grams of pure crystallized sulphate. It was slightly cloudy and could not be polarized with the greatest accuracy, but the reading was nearly 33°. A portion was heated one hour away from the air. It became clear and could be easily examined in the polarimeter, showing now at 20° in the 100 mm. tube 18.20°. This decrease is much less than in the other cases, but not unexpected.

FERROUS AMMONIUM SULPHATE.

The solution made contained in 100 cc., fifty grams of sugar and ten grams of the crystallized salt. When fresh it gave a rotation of 33.08°. After heating five hours to 71° the rotation was found to be 27.20°. This solution was allowed to stand in a stoppered bottle in the light and was polarized at different intervals with the following results:

July 24th	a_D	27.28°
Aug. 24th	"	20.22°
Oct. 22d	"	10.23°
Nov. 15th	"	7.53°

We have here, as before, a slow rate of inversion.

MANGANOUS CHLORIDE.

A solution was made on July 24th, containing in 100 cc. fifty grams of sugar and ten grams of the carefully purified salt with $4H_2O$. It gave immediately a rotation of 32.88°, and after heating five hours to 71° a rotation of 28.16°. From this date, July 24th, the heated portion was allowed to stand in the light at the laboratory temperature in a full bottle, and showed at intervals the following rotations, all in the 100 mm. tube, at 20°:

Aug. 24th	a_D	22.20°
Oct. 22d	"	4.71°
Nov. 15th	"	1.66°

After standing a short time in the light this solution became as colorless as water when observed in a clear glass bottle of four cm. diameter.

MANGANOUS SULPHATE.

The experimental solution was made to contain in 100 cc. fifty

grams of sugar and ten grams of crystallized manganous sulphate ($MnSO_4+4H_2O$). The rotation was found to be 33.16°. On heating the solution one hour to 100° it became slightly decomposed and darker in color, instead of lighter as with the chloride. The decomposition product was small in amount but exceedingly fine and dark. It remained long in suspension, making an exact reading of the rotation impossible. It was about +7°, however, in the 100 mm. tube. The suspended substance was probably an oxide of manganese.

ZINC SULPHATE.

A solution containing fifty grams of sugar and ten grams of the sulphate in 100 cc. showed when fresh a rotation of 32.98° for 100 mm. After heating forty-five minutes in boiling water the rotation was reduced to 18.42° for the same tube.

POTASSIUM ALUMINUM SULPHATE.

With a solution containing fifty grams of sugar and five grams of the alum in 100 cc. a rotation of 33° was found immediately. A portion was heated one hour in the water-bath to 100°, and on cooling to 20° was polarized again, showing now a rotation of −9.99. The heated solution became slightly cloudy, but the original remained clear through the severeal weeks it was kept.

LEAD NITRATE.

A fresh solution with 50 grams of sugar and ten grams of the salt in 100 cc. showed a rotation of 53.13°. A portion heated one hour to 100°, showed, after cooling to 20°, a rotation of −9.65° in the same tube.

LEAD CHLORIDE.

Some chloride was made by precipitation of the nitrate by sodium chloride. The product was recrystallized from hot water and washed repeatedly on a filter with cold water. About two grams of the moist precipitate was mixed with fifty grams of sugar in water enough to make ninety cc. and heated until it dissolved. On cooling the volume was made to 100 cc. A part of the chloride separated. The rotation was now found to be 23.52°. The mixture was shaken and a portion transferred to a flask with capillary stopper, where it was heated one hour to 100°. After cooling the rotation was found to be —7.53°.

CADMIUM CHLORIDE.

A fresh solution with fifty grams of sugar and eight grams of the chloride in 100 cc. gave a rotation of 32.91°. After heating to 100° it was reduced to —9.50°.

MERCURIC CHLORIDE.

The original solution of fifty grams of sugar and five grams of chloride in 100 cc. gave a rotation of 33.22°. A portion was heated an hour to 100° and became turbid, depositing on cooling a fine white precipitate. The clear liquid showed a rotation of —10.80°. A second portion was heated a shorter time, to the beginning of turbidity only. It was quickly cooled and polarized, showing a rotation of — 4.82°. By prolonged heating more of the precipitate is formed. It appears to consist of mercurous chloride only.

The salts tested above, while commonly called neutral, are those in which the base is very weak when compared with the acid. It is such salts that show in solution an acid reaction with certain indicators and the parallelism between the phenomena observed here and that of the inversion of sugar by acids naturally suggested itself. The following further test with a solution of ferrous iodide was therefore made. This solution contained in 100 cc. fifty grams of sugar and ten grams of the iodide. It polarized when fresh 32.41° in the 100 mm. tube. A number of small vials were nearly filled with this solution and they were heated in a thermostat through different times as shown below. The vials were made of selected glass, not readily attacked, and before use were heated some hours with hydrochloric acid. They were then washed and boiled with distilled water and dried. Before being placed in the thermostat they were closed with rubber stoppers having a capillary tube through the performation. The upper end of this extended above the water in the thermostat. The capillary opening was sufficiently fine to prevent any appreciable evaporation of the syrup while being heated. The water in the thermostat was kept at about 77.5°. Vials were removed from time to time and cooled quickly so that the contents could be examined in the polarimeter. The following results were found :

Time of heating in minutes.	Observed rotation.
0	32.41°
30	28.00°
60	26.25°
90	26.15°
210	24.61°
390	18.48°
570	16.60°
810	4.70°

These figures show a rapid, but an irregular change, in the rotation with the time, but as the temperature was not maintained with great accuracy, and as some of the vials were more exposed to the light than others, greater uniformity could not be expected.

To determine whether or not the inversion proceeds according to the law of Wilhelmy, a second series of experiments was made in which the temperature was carefully regulated and in which the small vials holding the sugar solutions were wrapped in tinfoil for protection against the light. The temperature in the last series of experiments was too low to permit them to be completed in a reasonable time. It was therefore brought to 87.5° for the following tests.

The amounts of sugar and ferrous iodide where the same as before, but greater care was taken in the preparation of the solution. Several samples of high grade commercial sugar were tested, and one was selected which satisfied all requirements as to purity. For 250 cc. of solution 125 grams of this sugar is dissolved in a small quantity of water in a graduated flask by aid of heat. Then 20.5 grams of the pure iodine, sublimed with potassium iodide, is weighed out and mixed in a flask with fifty cc. of water and seven grams of pure fine iron wire. The action of the iodine on the iron begins soon and must be checked after a time by dipping the flask in cold water. Finally when the action is practically complete, as shown by the disappearance of the iodine and change of color to greenish brown, the solution is boiled to make the reduction to the ferrous condition perfect. The amount of iron taken is largely in excess of that which can combine with the iodine. The ferrous solution is now allowed to cool to 50°–60° C. and filtered into the cooled sugar

solution made as above. The last traces of iodide from the flask and paper are washed down into the syrup by aid of a little boiled and cooled water. Finally the whole volume is made up to 250 cc. by the addition of distilled water. In this maner a solution is secured which contains in 100 cc., fifty grams of saccharose and ten grams of ferrous iodide, and which is practically free from inversion. The specific rotation of the strong pure syrup is 66.5°; that prepared with the iodide is 64.82°, as found from the mean of many closely agreeing determinations. It will be noted that this lower specific rotation is about the same as that found for the solutions of the other salts described above. The decrease in the rotation is apparently not a result of inversion.

The method of preparation of the syrup of ferrous iodide as described in the Pharmacopeia leaves a product slightly inverted because of the higher temperature of mixing the sugar and iodide solutions. When portions of the syrup made as just described are heated in boiling water an hour, in flasks with capillary stoppers to prevent evaporation, the rotation is reduced to — 11.5° at 20° for the 100 mm. tube. This value is almost identical with that calculated from the experiments of Gubbe,[1] *viz.*, — 11.31° for the rotation produced by the inversion of fifty grams of cane sugar in 100 cc. The presence of the excess of iodide seems to be without much influence on the specific rotation of the invert sugar.

In the experiments given below, the rotations were found in a 100 mm. tube at 20°. The reading before heating was 32.41°, and this is taken as the initial rotation instead of the theoretical 33.25°. Applying the Wilhelmy-Ostwald formula we have

$$\text{nat. log}\,\frac{A}{A-x} = Ct,$$

in which A represents the total amount of sugar present and may be measured by the total change in the rotation. It is therefore $32.41° - (-11.5) = 43.91°$. x represents the amount of sugar inverted at the time t, and is measured by the decrease in rotation at that time. $A - x$ represents the sugar remaining and the velocity of the inversion should be proportional to this.

[1] *Ber. d. chem. Ges.*, *1885*, 2207.

The table below gives the results of a series of experiments. The solutions were warmed two minutes before the counting of the times, t, began, as this was found necessary to bring them to the proper temperature. This, of course, introduces a small error into the calculation. The values in the fourth column are obtained by the use of common logaritims.

t min.	Observed rotation.	x	$\log \frac{A}{A-x}$	$\frac{1}{t} \log \frac{A}{A-x}$
30	28.50°	3.91°	0.04050	0.00135
60	24.85°	7.56°	0.08206	0.00137
120	17.80°	14.61°	0.17569	0.00146
180	13.35°	19.06°	0.24723	0.00137
240	6.32°	26.09°	0.39165	0.00163
300	4.32°	28.09°	0.44335	0.00148
420	−9.00°	41.41°	1.24461	0.00296

The results of the last column are sufficient to indicate that the inversion follows the general law shown by Wilhelmy to hold for the action of weak acids on sugar solutions. The values of $\frac{1}{t} \log \frac{A}{A-x}$ are not constant, but considering the conditions of the experiment, must be considered close enough until the last one is reached. The solution of the sugar is a very strong one containing fifty grams in 100 cc., and from such a degree of concentration no great regularity can be expected. The variation in the amount of water present as the saccharose becomes changed into dextrose and levulose must have some influence on the progress of the reaction, and one of the fundamental conditions of the Wilhelmy experiment is therefore not accurately observed. It has frequently been pointed out that the constant $\frac{1}{t} \log \frac{A}{A-x}$ may be quite irregular when calculated from tests on very strong solutions. The values are really constant only when the solvent is so greatly in excess that slight changes in it in the progress of the reaction, may be neglected. In the present case about two and five-tenths grams of water disappear in the formation of the new molecules, and this from a solution already very strong. Part of the irregularity in the constant may doubtless be explained in this manner. An accidental exposure to light during the last interval of the heating may partly account for the change in the last value.

It has been found by later experiments, some of which are still in progress, that with dilution of the solutions much more uniform results may be secured, approaching, in fact, those obtained from the action of weak acids alone.

The cause of the inversion of strong sugar solutions by these heavy salts is undoubtedly to be found in their condition of partial hydrolysis by the solvent. The acid ion in each case is a strong one, while the basic ions are all relatively weak. Indeed, it has been suggested by Walker and Aston[1] that the amount of hydrolysis in solutions of certain salts may be approximately measured by comparing the speed of inversion with that of known amounts of weak acids. The method can be easily applied to a large number of solutions of moderate concentration. Further investigations with special reference to ferrous salts are now in progress.

CHICAGO, DECEMBER, 1895.

MIXED DOUBLE HALIDES OF PLATINUM AND POTASSIUM.

BY CHARLES H. HERTY.
Received November 16, 1895.

INTRODUCTION

BY mixing together water solutions of platinum chloride and potassium bromide in the proportion of one molecule of platinum chloride to two molecules of potassium bromide, Pitkin obtained[2] a compound having the composition represented by the formula $K_2PtCl_4Br_2$.

Two possible explanations were advanced by Pitkin,

$$(1)\quad PtCl_4 + 2KBr = K_2PtCl_4Br_2,$$

a true chemical compound being formed; or

$$(2)\quad 4KBr + 3PtCl_4 = 2K_2PtCl_6 + PtBr_4$$
$$PtBr_4 + 2KBr = K_2PtBr_6,$$

giving thus an isomorphous mixture of K_2PtCl_6 and K_2PtBr_6. In either case the percentage of the elements remains the same. To determine which of the two explanations is correct, he resorted to fractional crystallization, and from the above solu-

[1] *J. Chem. Soc.*, July, 1895.
[2] This Journal, 1, 472.

tion obtained three successive crops of crystals. Determinations of platinum in each of these showed that they were identical, and he concludes, therefore, that the substance is a chemical compound and not an isomorphous mixture.

In a second paper[1] he described the series

K_2PtBr_5Cl
$K_2PtBr_4Cl_2$
$K_2PtBr_3Cl_3$
$K_2PtBr_2Cl_4$
$K_2PtBrCl_5$.

These were prepared by mixing together stated quantities of K_2PtCl_6 and K_2PtBr_6, dissolving in water and crystallizing. Three successive crops of K_2PtCl_5Br were obtained, showing respectively 36.97, 37.04 and 36.99 per cent. of platinum, again confirming the idea that these substances were true chemical compounds.

In the discussion, which followed the reading of the paper, Dr. Endemann suggested that these substances were most probably isomorphous mixtures.

In a third paper[2] Pitkin discussed the question of isomorphism and fractional crystallization, upholding his formerly expressed view that the platinum compounds were true chemical compounds. His argument was:

1. In isomorphism "the resulting mixed crystal has a composition dependent on the ratio, one to the other, of the isomorphous salts in solution or the constituents forming these salts."

2. "When two isomorphous salts together in solution are subjected to fractional crystallization, the salts differing in their degree of solubility in the menstruum employed, the crystals first formed will contain relatively a greater amount of the more insoluble salt, while the crystals formed at the end will be correspondingly rich in the more soluble salt."

It is principally upon the second consideration that he bases his claim that the substances are true chemical compounds and not isomorphous mixtures. This claim has been generally accepted and we find in many text books descriptions of the salt $PtCl_4.2KBr$.

[1] This Journal, 2, 296.
[2] *Ibid.*, 2, 408.

Quite recently Pigeon[1] has prepared a substance to which he gives the formula $K_2PtCl_2Br_4$. He considers it one of the series previously prepared by Pitkin.

During the past few years I have been constantly occupied with efforts to prepare double halides containing more than one halogen. I have shown[2] that the double halides of lead and potassium and of antimony and potassium containing more than one halogen are isomorphous mixtures of the double halides containing one halogen. It has seemed desirable, therefore, to repeat the work of Pitkin and determine whether the facts upon which he based his reasoning are correct.

I may state in advance that his analytical results are altogether inaccurate and inadequate. The reasoning which he makes use of to prove that the substances are true chemical compounds, proves beyond doubt, when interpreted by the results which I have obtained, that the substances are isomorphous mixtures.

METHOD OF ANALYSIS.

In the analyses of his compounds Pitkin determined platinum alone. These determinations were made by heating the substance with oxalic acid, thoroughly washing the residue and weighing the dried spongy platinum.

Deeming the determination of platinum alone insufficient, I have analyzed all the compounds prepared during this investigation by reduction in hydrogen.

The hydrogen, generated in a Kipp apparatus, was purified by being passed through an acid solution of potassium permanganate, over moist copper carbonate, through alkaline permanganate solution, through water, and finally over calcium chloride, in the order named. The gas was then passed through a combustion tube, about twelve inches in length, in which was placed a porcelain boat containing a weighed quantity of the substance to be analyzed. The combustion tube, constricted at the end, was closely connected with a U tube, in turn connected with another U tube, both tubes containing potassium hydroxide solution. Before analysis the dried crystals were finely powdered and thoroughly dried at 110°. After placing in the combustion

[1] *Ann. chim. phys.* [7], 2, 433.
[2] *Am. Chem. J.*, 15, 81, and 16, 490.

tube the boat containing the substance to be analyzed, all air was driven out by the current of hydrogen. Gentle heat was then applied by means of a Bunsen burner with a winged top attachment. As the reduction proceeded the heating was slowly increased until the flame from the burner almost touched the tube. This was maintained for some time. Finally the flame was removed and the tube allowed to cool, hydrogen passing through for one hour longer in order to remove all traces of hydrochloric or hydrobromic acids. The liquid in the U tubes was then transferred, with thorough rinsing, into a beaker and dilute nitric acid added in excess. The boat containing the metallic platinum and the potassium salts was removed from the tube and the mass thoroughly extracted with water by standing twenty-four hours. The platinum was then filtered in a porcelain Gooch crucible and thoroughly washed with water.

The crucible was then dried for one hour in an air-bath at 110°, heated to redness in a platinum crucible, allowed to cool, and weighed, the platinum being in the form of gray metal. In the filtrate from the platinum and in the neutralized liquid from the U tubes bromine and chlorine were determined by addition of an excess of standard solution of silver nitrate, filtering the precipitated silver halides in porcelain Gooch crucibles, and titrating the excess of silver in the filtrates with a standard solution of ammonium thiocyanate. The crucibles containing the silver salts were dried for three hours at 150°. From the weight of silver used and the weight of silver halides in the Gooch crucibles the weights of bromine and chlorine were calculated. In several cases the neutralized liquid from the U tubes was added to the filtrate from the platinum, the total bromine and chlorine being determined at one time.

In one salt potassium was determined as potassum sulphate by first removing the platinum by electrolysis, then evaporating with sulphuric acid in a weighed platinum dish.

In all of the analytical work vessels were allowed to stay on the balances ten minutes before being weighed. The atomic weights used were: platinum 194.34, potassium 39.03, chlorine 25.37, and bromine 79.76.

The above method of analysis is open to several criticisms:

In the first place the sodium nitrate in the neutralized liquid from the U tubes dissolves a small portion of the precipitated silver salts. In the second place, it is very difficult to remove all of the hydrochloric or hydrobromic acids from the finely divided platinum either by heating or by extraction with water.

In spite of these errors this method would seem to yield much more reliable results than the method of heating with oxalic acid, applicable for determinations of platinum alone.

PREPARATION OF MATERIALS.

The potassium bromide used in this investigation was heated sufficiently high to decompose any potassium bromate present and to drive off any ammonium chloride, repeatedly recrystallized from water, dried, finely powdered, and again thoroughly dried. Potassium chloride was prepared in the same manner.

Great difficulty was experienced in the preparation of pure chloroplatinic acid. This was unexpected, as previous investigators make no mention of any great difficulty. The purest specimens sent out by the manufacturers showed, on reduction in hydrogen, a coating of ammonium chloride on the combustion tube after raising the heat considerably. The substance was then prepared by dissolving platinum in aqua regia and evaporating repeatedly with hydrochloric acid. Still ammonium chloride was found after reduction with hydrogen. The constant appearance of ammonium chloride led to the hypothesis that some nitrogen compound might be present in the hydrogen used, and on coming into contact with the platinum black, in the presence of hydrogen and hydrochloric acid, might be converted into ammonium chloride. To test this point hydrogen was prepared from strictly pure zinc and the purest sulphuric acid which could be obtained. This hydrogen was then purified by Phillips' method.[1] Still ammonium chloride appeared after reduction of the platinum compounds.

The next explanation which suggested itself was the presence of some trace of the compound $2NOCl.PtCl_4$, formed during the treatment with aqua regia. To elminate this possible source of error, chloroplatinic acid was prepared by the method recommended by Pigeon,[2] in which no nitric acid is used. This

[1] *Am. Chem. J.*, 16, 165.
[2] *Am. chim. phys.* [7]. 2, 403.

method consists in precipitating the platinum as ammonium platinichloride, reducing this at a low temperature in hydrogen, and treating the finely divided platinum with hydrochloric acid and chlorine in a large flask, the chlorine being replenished as rapidly as it is taken up by the platinum.

A specimen prepared in this way also yielded ammonium chloride. While repeating this method of preparation an accident showed its unfitness for the purpose. According to directions a portion of the ammonium platinichloride had been reduced in hydrogen at a temperature just sufficient for the reduction, and the ammonium chloride evolved driven from the tube. Accidently the temperature was considerably raised. Immediately quite a large deposit of ammonium chlorine was formed on the combustion tube, showing that platinum black occludes ammonium chloride in quite large quantity. Efforts were made to remove all of the occluded ammonium chloride by prolonged heating in hydrogen but this proved very unsatisfactory. This method of Pigeon's is therefore unfit for use and there is little doubt but that the substances with which he conducted his thermochemical experiments were largely contaminated by ammonium platichloride. A second method of Pigeon's was then tried. This consists in passing a current of chlorine gas through an emulsion of ammonium platinichloride and hot water. Nitrogen is given off and chloroplatinic acid formed, but on reduction in hydrogen ammonium chloride was again deposited. Finally, at the suggestion of Dr. H. N. Morse, of Johns Hopkins University, ammonium platinichloride was intimately mixed with pure oxalic acid and the mass heated to redness. A residue of spongy platinum was oblained which gave only a slight deposit of ammonium chloride on being heated in hydrogen. The platinum thus prepared was converted into chloroplatinic acid by treatment with chlorine and hydrochloric acid. The hydrochloric acid was prepared by heating concentrated chemically pure hydrochloric acid and passing the liberated gas into freshly distilled water. The chloroplatinic acid thus prepared still yielded a slight deposit of ammonium chloride.

Further attempts were made to purify this by cooling the solution, in the hope that the ammonium platinichloride would sepa-

rate from the solution, but this failed. Finally a current of chlorine gas was passed through a portion of this chloroplatinic acid solution for some time. The product still yielded a slight quantity of ammonium chloride on reduction in hydrogen. However, it was considered sufficiently pure for the purposes of the investigation and accordingly was used. All of the above processes were carried out in a room as free from ammonium chloride as was practicable.

The amount of platinum in the water solution of the chloroplatinic acid was determined by electrolysis.

One cc. solution = 0.08956 gram of platinum.

The use of chloroplatinic acid for determining potassium suggests that in addition to the precautions, already taken by the Association of Official Agricultural Chemists, of working in a room other than the general laboratory, more care should be taken in regard to the adsence of ammonium platinichloride from the chloroplatinic acid as first sent out by the manufacturers.

METHOD OF WORK.

If the substances obtained by Pitkin are true chemical compounds it seems only natural to suppose that they could be reproduced under at least some slight variation in the original proportions of the substances used in their preparation. To determine this point four solutions were prepared, using the same amount of platinum solution in each. In one a definite quantity of potassium bromide was used. In the other three arbitarily taken portions of the potassium bromide were replaced by equivalent quantities of potassium chloride. To prepare $K_2PtCl_4Br_2$, Pitkin used two grams platinum chloride and 1.404 grams of potassium bromide. These are the quantities required by using the atomic weights: platinum 197.18, chlorine 35.46, bromine 79.95, and potassium 39.13. More recent determinations of the atomic weight of platinum give the figure 194.34. The above quantities therefore evidently do not give the proportion $PtCl_4 : 2KBr$. However I have endeavored to meet this point by using 1.404 grams of potassium bromide and 12.99 cc. of platinum solution = 1.163 grams of platinum, conforming thus to the proportion $PtCl_4 : 2KBr$ according to the atomic weights used by Pitkin.

In the replacement of potassium bromide by potassium chloride the more recent atomic weights were used. Potassium 39.03, chlorine 35.37. and bromine 79.76.

The quantities of the various substances actually used in the four experiments were:

TABLE I.

	H_2PtCl_6 Sol. cc.	H_2O. cc.	KBr. Grams.	KCl. Gram.
A	12.99	57.00	1.404	......
B	12.99	57.00	1.200	0.1278
C	12.99	57.00	1.000	0.2531
D	12.99	57.00	0.800	0.3784

When the two solutions in each case were first mixed a small quantity of a light yellow precipitate was thrown down. On boiling with an inverted condenser all dissolved, the solutions becoming dark red. After cooling bright red octahedral crystals separated in each case, growing slightly lighter in color from A to D. The crystals were prepared for analysis as described above. On analysis the following results were obtained:

TABLE II.

	Pt. Per cent.	Cl in distillate. Per cent.	Br in distillate. Per cent.	Cl in residue. Per cent.	Br in residue. Per cent.	Total Cl. Per cent.	Total Br. Per cent.
A	34.93	23.19	4.47	4.74	18.12	27.93	22.59
B	35.90	24.91	2.03	6.19	15.47	31.10	17.50
C	36.46	26.02	1.04	7.58	12.93	33.60	13.97
D	37.07	26.73	0.31	8.41	11.44	35.14	11.75

TABLE III.

	Calculated for $K_2PtCl_4Br_2$.	A	B.	C.	D.	Calculated for K_2PtCl_5Br.
Pt per cent	33.89	34.93	35.90	36.46	37.07	36.74
Cl " "	24.67	27.93	31.10	33.60	35.14	33.43
Br " "	27.82	22.59	17.50	13.97	11.75	15.08
Atomic ratio						
Pt: (Cl + Br)	....	1:5.97	1:5.95	1:6.00	1:5.98	....

From these results it is evident that four substances have been prepared, each differing in composition from the two nearest members of the series described by Pitkin, $K_2PtCl_4Br_2$ and K_2PtCl_5Br.

Furthermore the crystals show a variation in composition in

accord with the variation in composition of the solutions from which they formed. (See Table I). Yet in all four substances the atomic ratio of platinum to chlorine and bromine combined is practically 1 : 6. Again, if we assume C to be an isomorphous mixture of K_2PtCl_6 and K_2PtBr_6, then 33.60 per cent. of chlorine requires 30.77 per cent. of platinum, while 13.97 per cent. of bromine requires 5.68 per cent. of platinum, giving the total per cent. of platinum required by this assumption 36.45. There was actually found 36.46 per cent.

In the hope of gaining some light upon the nature of these substances, separate determinations of chlorine and bromine were made in the portion which passed off in the current of hydrogen and in the portion combined with potassium in the residue. No definite conclusion on this point can be drawn from the results, except that a portion of the hydrobromic acid liberated decomposed a portion of the potassium chloride, setting free hydrochloric acid. Thermochemical considerations lead us to expect this as has been pointed out already by Pigeon. The results in Table III seem to show that the substances are isomorphous mixtures.

Pitkin's principal argument in support of the idea that the substances obtained by him were true chemical compounds is that the successive crops of crystals obtained from a solution of platinum chloride and potassium bromide are identical. Three successive crops were analyzed by him and gave the per cents. of platinum respectively, 34,22, 34.70, and 34.39. No determination of bromine or chlorine was made. To test this point more thoroughly the mother-liquors from A, B, C, and D above were evaporated to about one-half of the previous volume and allowed to crystallize. Crystals were obtained in each case closely resembling the first crops obtained from the respective solutions. These crystals, desiginated A′, B′, C′, D′, gave on analysis:

TABLE IV.

	Pt. per cent.	Cl. per cent.	Br. Per cent.	Atomic ratio. P : (Cl + Br).
A′	33.48	25.37	26.26	1 : 6.08
B′	34.10	26.14	25.58	1 : 6.04
C′	35.27	28.30	22.25	1 : 5.95
D′	36.10	31.63	17.09	1 : 5.97

Potassium was determined in A′. There was found 13.59 per cent.

Finally the mother liquors from A′, B′, C′, and D′ were allowed to evaporate spontaneously until all water had passed off. A third crop of crystals was thus obtained in each case. These crystals closely resembled the former crops in regard to crystal form, but were much darker in color. They were designated A″, B″, C″ and D″.

A slight odor of hydrochloric or hydrobromic acid was noticed in each vessel when the evaporation was complete. On analysis the substances gave the following :

TABLE V.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio. Pt : (Cl + Br).
A″	32.76	20.53	33.14	1 : 5.91
B″	32.88	22.30	31.36	1 : 6.05
C″	34.35	26.44	24.21	1 : 5.95
D″	35.09	28.01	22.20	1 : 5.93

By combining Tables II, IV and V it will readily be seen that the successive crops of crystals obtained from a solution are by no means identical, thus:

TABLE VI.

	Pt. per cent.	Cl. per cent.	Br. per cent.
A	34.93	27.93	22.59
A′	33.48	25.37	26.26
A″	32.76	20.53	33.14
B	35.90	31.10	17.50
B′	34.10	26.14	25.58
B″	32.88	22.30	31.36
C	36.46	33.60	13.97
C′	35.27	28.30	22.25
C″	34.35	26.44	24.21
D	37.07	35.14	11.75
D′	36.10	31.63	17.09
D″	35.09	28.01	22.20

If these results be arranged according to the per cent. of platinum, it will be seen that twelve substances have been prepared, each varying from the calculated per cents. for $K_2PtCl_4Br_2$ or K_2PlCl_5Br, yet approaching these more nearly than any of the

other members of the series prepared by Pitkin. In all of the twelve the atomic ratio of platinum to chlorine and bromine combined, allowing for error in the analytical work, is practically 1 : 6, which is required if the substances are isomorphous mixtures :

TABLE VII.

	Pt. per cent.	Cl. Per cent.	Br. Per cent.	Atomic ratio Pt : (Cl + Br).
A″	32.76	20.53	33.14	1 : 5.91
B″	32.88	22.30	31.36	1 : 6.05
A′	33.48	25.37	26.26	1 : 6.08
B′	34.10	26.14	25.58	1 : 6.04
C″	34.35	26.44	24.21	1 : 5.95
A	34.93	27.93	22.59	1 : 5.97
D″	35.09	28.01	22.20	1 : 5.93
C′	35.27	28.30	22.25	1 : 5.95
B	35.90	31.10	17.50	1 : 5.95
D′	36.10	31.63	17.09	1 : 5.97
C	36.46	33.60	13.97	1 : 6.00
D	37.07	35.14	11.75	1 : 5.98

In addition to these, five other compounds were prepared. In these platinum was determined by electrolysis.

The per cents. of platinum found in these were 35.05, 34.94, 34.43, 34.00, and 33.26.

Pitkin relied upon analytical data in which no attention was paid to a variation of one-half per cent. and in one case one per cent. in the amounts of platinum present in different substances. Such were considered identical. By an inspection of Table VII it will be seen that such a variation in the platinum means so great a variation in the chlorine and bromine that it is impossible to consider such substances identical.

From the above evidence there seems little doubt but that the substances are isomorphous mixtures. To test the point still further a large portion of A was dissolved in hot water : on cooling, crystals quite similar to A separated. These were dried and designated X. The analytical results are placed side by side with those of A for convenience in comparing the two.

TABLE VIII.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio Pt : (Cl + Br).
A	34.93	27.93	22.59	1 : 5.97
X	35.48	29.96	18.80	1 : 5.93

By recrystallization the first crop obtained was thus evidently richer in the more insoluble compound, K_2PtCl_6. This would be expected in the case of an isomorphous mixture of two substances differing in their degree of solubility.

Further evidence of the mixed nature of the substances was obtained by placing a considerable quantity of the substance X in a well fitting glass stoppered bottle, pouring upon the finely powdered substance a quantity of water quite insufficient for complete solution in the cold, placing the stopper in the bottle and shaking thoroughly several days. After being shaken for a short time and the undissolved portion allowed to settle, it was found that instead of the homogeneous powder, originally present in the bottle, two distinct layers were now present, one a dark red, the other a light yellow. Evidently the water had dissolved the more soluble red bromide to a larger extent than the less soluble yellow chloride. After four days the liquid was filtered from the undissolved residue. This residue was thoroughly dried, powdered, and intimately mixed and labelled Y. Its analysis, compared with the original substance X showed

TABLE IX.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio Pt : (Cl + Br).
X..........	35.48	29.96	18.80	1 : 5.93
Y..........	35.87	30.98	17.80	1 : 5.96

confirming thus the idea that the more soluble bromide had dissolved to a larger extent than the less soluble chloride.

SUMMARY.

Four lines of evidence have thus been adduced, all pointing to the conclusion that the double halides of platinum and potassium containing more than one halogen are isomorphous mixtures of different double halides containing only one halogen:

1. The formation of a series of substances varying in composition approximately as the variation in the composition of the solutions from which they crystallized. None of these substances correspond to the formulas proposed by Pitkin, but all show an approximate atomic ratio, platinum to chlorine and bromine, of 1 : 6. Fifteen other substances, all varying in composition, have been prepared; in ten of these the atomic ratio of platinum

to chlorine and bromine was found to be practically 1 : 6, in th other five platinum alone was determined.

2. The successive crops of crystals obtained from a wate solution of chloroplatinic acid and potassium bromide are nc identical, but show gradually increasing proportions of th more soluble potassium platinibromide and correspondingl decreasing proportions of the less soluble potassium platini chloride.

3. On recrystalling from water one of the substances unde examination, the first crop of crystals is not identical with th original substance but is a product richer in chlorine and corres pondingly poorer in bromine. This is to be expected on recrys tallizing an isomorphous mixture of two substances differing i degree of solubility.

4. On treating one of the substances obtained with a quantit of water insufficient for complete solution, the more soluble bro mide was dissolved from the mass to a greater extent than th less soluble chloride. This was confirmed both by the appear ance of the insoluble residue and its analysis.

At the beginning of this investigation Mr. Henry Hillyer, Jr. a student in this laboratory, was associated with me in the work His sad death at his home in Augusta, Ga., on April 4, 1895 terminated this association. I desire to here pay tribute to hi rare qualifications as an investigator and to the manliness whicl characterized his every act.

UNIVERSITY OF GEORGIA,
NOVEMBER 9, 1895.

THE QUALITATIVE EXAMINATION OE ACETANILID.

BY CHARLES PLATT.

Received November 22, 1895

IN view of the deficiency in the analytical literature o the acid anilids the following tests may prove of interest The formation of acetanilid, or phenylacetamid, $C_6H_5NHC_2H_3O$ from anilin and glacial acetic acid

$$C_6H_5NH_2 + C_2H_3O.OH = C_6H_5NHC_2H_3O + H_2O,$$

and the corresponding formation from anilin and acetyl chlo ride

$$C_6H_5NH_2 + C_2H_3OCl = C_6H_5NHC_2H_3O + HCl,$$

suggest the adaptability of various color reactions with the acids and alkalies. The physical constants have been determined and the decomposition of the anilid made to serve for its identification.

Acetanilid is a white crystalline powder neutral in reaction and tasteless but producing a slight burning sensation when placed upon the tongue. Examined under the microscope it is found to be made up of broken crystalline plates. The melting point, commonly given as 113°–114°, is determined by the writer as fairly constant at 112°. Heated on platinum, acetanilid volatilizes without leaving a residue, and, when ignited, it burns completely with a yellow flame. At 15° it is soluble in about 190 parts of water and in five parts of alcohol. It is soluble in eighteen parts of boiling water and in about five-tenths part of boiling alcohol. It is soluble in the cold in ether, chloroform, acetic acid, nitric and sulphuric acids, and ,when warmed, in hydrochloric acid. On boiling with water, oil-like globules separate out and the solution on cooling recrystallizes in large but delicate six-sided plates.

Reaction with Concentrated Nitric Acid.—Acetanilid is easily soluble in strong nitric acid, the solution being colorless in the cold but turning to a yellow, then brownish red, on gentle warming, nitrogen oxides being at the same time evolved. The colorless solution on standing in the cold gradually acquires a light green tint but finally changes, through yellow, to red, with formation of red acicular crystals. This red solution gives off the odor of nitrobenzene. A similar appearance and odor are produced by evaporating nitric acid solutions ; an oily residue of decided odor being produced by rapid evaporation, a crystalline residue of slight odor by slow evaporation. The nitric acid solution has been described by one writer as colorless; by another as brown, then blue, then colorless.

Reaction with Dilute Nitric Acid.—The acetanilid is slowly soluble in the cold, and without change in color but with separation of oil-like globules. This solution on slow evaporation gives a brown residue with slight purplish tint. By boiling with diiute nitric acid a colorless solution is obtained, with evolution of pungent fumes.

Reaction with Concentrated Sulphuric Acid.—A colorless solution is formed, unaffected by heating to boiling. The solution in cold concentrated acid, on long standing, acquires a pink to brown color. With an excess of the acetanilid the pink coloration develops quickly, is well marked, and changes gradually to an orange by reflecting light. As a final change tufts of delicate acicular crystals appear and the solution gradually becomes colorless.

Reaction with Sulphuric Acid and Potassium Chromate.—A solution in concentrated sulphuric acid is turned to a dark green on addition of a few drops of potassium chromate. A solution in concentrated sulphuric acid, subsequently diluted, gives no reaction at first with the potassium chromate but on standing is gradually turned to a reddish-brown, and finally to a dark olive-green. A similar reaction to the last is produced by addition of the chromate to a solution in cold dilute acid.

Reaction with Hydrochloric Acid.—The acetanilid easily dissolves in hydrochloric acid when warmed and no precipitate is produced by subsequent dilution with water.

With hydrochloric acid and potassium dichromate there is no well marked reaction.

Reaction with Hydrochloric Acid and Potassium Permanganate.—An olive-green coloration is obtained by adding a small crystal of the potassium permanganate to the solution in hydrochloric acid. On standing the color is changed to a mahogony-brown.

Reaction with Hydrochloric Acid and Chromic Acid.— A solution of acetanilid in hydrochloric acid, diluted, and treated with a weak solution of chromic acid gives a yellowish-green coloration, which gradually turns to a dark green. Potassium hydroxide produces a blue precipitate in this solution.

Reaction with Hydrochloric Acid and Bromine.—Bromine water added in excess to a solution in hydrochloric acid produces a heavy yellow to white precipitate of the monobrom derivative of anilin. This precipitate examined microscopically is found to be made up of a fine interlacing net-work of needles or fiber-like crystals. A similar precipitate is obtained by means of bromine water in a water solution of the acetanilid.

Reaction with Hydrochloric Acid and Chlorine.—Chlorine water

added to a solution in hydrochloric acid gives a dark blue coloration which afterwards fades. A similar reaction is obtained by substituting for the chlorine water a filtered solution of bleaching powder.

Mercuric chloride added to the hydrochloric acid solution gives no precipitate.

Dissolve some of the powder in a little hydrochloric acid and add, first, a few cc. of five per cent. phenol, then a little clear saturated solution of chlorinated soda or lime. The solution acquires a brownish-red color turning to a blue on addition of ammonium hydroxide in excess.

Reaction with Potassium Hydroxide.—By heating some of the powder with potassium or sodium hydroxide the characteristic odor of anilin is developed.

Reaction with Potassium Hydroxide and Chloroform.—By heating with potassium or sodium hydroxide and a few drops of chloroform the characteristic odor of an isonitrile is developed, phenylisocyanide being formed.

Reaction with Sodium Nitrate and Sulphuric Acid.—The powder mixed with sodium nitrate and sprinkled upon concentrated sulphuric acid produces a fine red coloration.

Reaction with Ferric Chloride.—A cold saturated water solution added to neutral ferric chloride produces no change in color.

Reaction with Zinc Chloride.—Acetanilid heated to 270° with an equal weight of zinc chloride produces, first orthoamidoacetophenone, in small amount, and then flavanilin $C_6H_{14}N_2$, a yellow substance with a green fluorescence, a derivative of quinolin. It is stated in a number of text-books that acetanilid boiled with zinc chloride, anilin, and acetic acid will produce amidoacetophenone, $C_6H_4NH_2C_2H_3O$, but this test is untrustworthy inasmuch as the regents used will produce this substance in absence of acetanilid. The paramidoacetophenone produced is crystalline in nature, while the ortho derivative formed in the previous test by heating zinc chloride and acetanilid in a yellow oil of high boiling point and with a characteristic sweetish odor.

Reaction with Plugge's Reagent.—Boil the acetanilid with water, cool and filter off if necessary, then boil again with potas-

sium nitrite and dilute nitric acid. Mix with Plugge's reagent, a solution of mercurous nitrate with a little nitrous acid, and again heat to boiling. A deep red color is developed.

Antipyrin and phenacetin, two other popular antipyretics much used in medicine, may be readily distinguished from acetanilid by the foregoing tests. Antipyrin, for instance, with ferric chloride gives a deep-red coloration and is precipitated from its solutions by mercuric chloride. It has approximately the same melting point as acetanilid, but, unlike the latter, is decomposed by further heating. The characteristic reactions for phenacetin have been given by the writer in a former article.[1]

Comparative tests have been made upon various samples of acetanilid of domestic and foreign manufacture. The products of reputable houses seem to be practically identical with the exception of difference in perfection of crystallization and a corresponding difference in appearance.

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HEATS OF SOLUTION OF SOME CARBON COMPOUNDS.

BY C. L. SPEYERS.

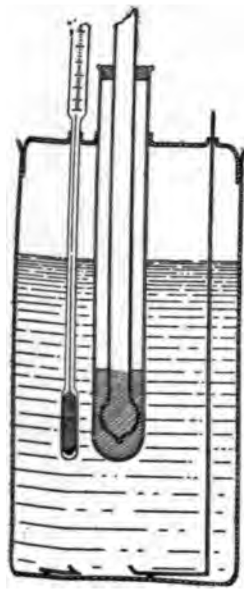
Received October 14, 1895.

THE following paper contains a few data about the heats of solution of some solid carbon compounds in water, methyl alcohol, ethyl alcohol, propyl alcohol, chloroform, and toluene.

The simple method given by Nernst[2] was used.

The calorimeter was made of thin glass. The rim was ground to take the cover which fitted fairly well against the inside ground rim of the beaker, not air tight but tight enough to prevent appreciable evaporation of the more volatile solvents during the experiment. The cover had three holes with short tubulures. The center tubulure carried a test-tube firmly fastened with a cork, the second tubulure as close to the center one as possible, carried the thermometer, while the third one, somewhat farther from the center, let the handle of the platinum stirrer pass through; see figure. The calorimeter held com-

[1] *J. Anal. Appl. Chem.*, 7, 2.
[2] *Ztschr. phys. Chem.*, 2, 23.



fortably 375 cc., none of the liquid spattering against the cover while stirring. In calculating the water value of the calorimeter, the cover, being some distance from the surface of the solution, was not considered; as the calorimeter without the cover weighed 64.70 grams, its value was $64.70 \times 0.195 = 12.63$ grams. Later on this calorimeter was broken and replaced by another whose value was $69.44 + 0.195 = 13.54$ grams water. The first calorimeter with cover weighed 87.60 grams, the second one, 94.90 grams.

The bottom of the test-tube which held the substance to be dissolved was about two inches below the surface of the solvent. A glass tube closed at both ends and blown out a little at one end, projected above the projecting vessels of the calorimeter and ran down to the bottom of the test-tube. A sharp tap on the top shattered the bottom of the test-tube and the solvent entering quickly dissolved the solid when the latter was rubbed off the sides of the test-tube by the swelled tube. This was quite necessary, for the finely powdered solids made a pasty mass with the solvent and stuck tenaciously to the test-tube.

The test-tube were so near the same size and dipped so equally into the solvent that the water value of this part could be considered constant. In a few exceptional cases the test-tubes were of a different size. The same plunger was used throughout.

The platinum stirrer was made of ordinary laboratory foil stiffened with wire. It was disk-shaped and about nine cm. in diameter. From the circumference inward, about one cm., and then parallel with the circumference about two cm., cuts were made. The pieces thus partly cut loose were bent alternately up and down. A stout platinum wire was welded to the

disk, and ended in a cork, to serve as a non-conducting handle. A circular hole in the center let the thermometer and test-tube pass through. This stirrer has already been described in the chemical literature;[1] it was very effective. Its total weight, without cork, was 12.036 grams, but as only 9.948 grams dipped into the liquid, its value was taken to be $9.948 \times 0.0324 = 0.322$ gram of water.

The thermometer was made by Götze some seven years ago. It was divided into hundredths of a degree and thousandths could easily be estimated when observing through a telescope. Its value was determined by cooling in ice and plunging into the calorimeter, as well as by measurement and computation; it was 1.0 gram water. It was carefully calibrated.

The solutions were so dilute, their specific heats could be reasonably considered equal to those of the pure solvents.

The calorimeter stood on three hard wood pins in a bright tin vessel, large enough to leave an air space of an inch all around. The sides and top of the tin vessel were covered with felt. This tin vessel in turn stood on three pins in another bright tin vessel, leaving an air space of two inches all around. The sides and top of this tin vessel were likewise covered with felt. In turn, it stood in a third bright tin vessel, leaving an air space of two inches all around. This last vessel had only a top cover of felt. It was immersed to within an inch of the top in water contained in a large galvanized tank about seventy-five cm. in diameter and thirty cm. deep. The temperature of the water was kept around 25°.

These arrangements were required because the experiments were carried on at night in a small room and the abundant radiation had to be checked. They answered the purpose.

The solvent was contained in a calibrated flask. This stood on a piece of felt in a bright tin vessel, whose sides and top were covered with felt. This vessel in turn stood on three hard wood pins in another bright tin vessel which had only a top cover of felt because it was immersed to within an inch of the top in the water of the large tank just mentioned. The flask was carefully calibrated for delivery. It had a long neck with a felt wrapping

[1] I cannot recall where.

to protect against the heat of the hand when pouring out the solvent.

Some hours before an experiment was to be made the flask was filled and put in the proper vessel in the tank. The calorimeter, with substance in the test-tube, and test-tube, thermometer, and stirrer, in place, was also put in the proper vessel in the tank. When the time came, the solvent was carefully poured into the calorimeter and the apparatus put together again. The mercury in the thermometer soon assumed a slow, regular motion. Observations were then made every minute for five minutes, at the same time the liquid was stirred slowly and regularly. At the end of the fifth minute a sharp tap on the projecting glass tube shattered the bottom of the test-tube and a few up and down rubs removed the pasty mass from the walls of the tube. The stirring was kept up all the time, slowly and regularly. The solution was generally completed within a minute, but in any case, no more than five minutes were required for complete solution. The mercury then resumed the previous slow and regular movement. The beginning of this regular movement was sharply marked and showed when solution was complete. The mercury was again observed every minute for another five minutes. The change in temperature from the time of adding the solid to the time of slow and regular movement was considered as the change in temperature produced by dissolving the substance.

The corrections were calculated by Regnault's and Pfaundler's method.[1]

In the following tables, these abbreviations are used :

m = mass of substance dissolved in grams.

Δt^1 = average change in temperature for one minute during the first five minutes.

Δt^2 = ditto during the second five minutes.

t = correction.

ΔT = corrected change in temperature produced by dissolving the substance.

M = value in grams of water, of liquid, calorimeter, thermometer, test-tube, and plunger.

[1] See Berthelot : Calorimetrie chimique, p. 41.

q = quantity of heat in small calories connected with the solution of m grams of substance.

Q = quantity of heat in small calories connected with the solution of one gram molecule of substance.

T = temperature of solvent at commencement of experiment.

HEATS OF SOLUTION IN WATER.

The water was carefully distilled, but was not further purified.

Urea.

The urea came from Merck; it was recrystallized from alcohol, powdered, and dried. Melting point = 132.7° cor.; melting point according to Beilstein = 132°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.2909	+0.0008	—0.0018	—0.004	—0.518	389.4	—201.7	—3690	24.5°
1.1498	—0.0014	—0.0014	—0.001	—0.176	389.6	— 68.57	—3577	24.2°

Average, —3628.5 cals.

Thomsen gives 3349 calories; Ostwald, quoting Berthelot and Petit, gives 46 K, where K may be considered as 100 calories.

Urethane.

The urethane came from Kahlbaum. Melting point = 48.5° cor. It was melted, dried and powdered. Melting point = 47.33° cor. Tested for chlorine, but none found.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
4.3687	—0.0026	—0.0048	—0.005	—0.479	388.4	—186.6	—3801	22.5°
0.9380	—0.0026	—0.0020	—0.002	—0.102	389.8	—39.74	—3773	23.5°

Average, —3787 cals.

Chloral Hydrate.

From Kahlbaum. Aqueous solution slightly acid. On adding silver nitrate and nitric acid to an aqueous solution, a slight precipitate formed after twenty-four hours. Concentrated sulphuric acid caused the separation of chloral, without any coloration. Melting point = 49.4° cor. Beilstein quotes melting point = 57°; Fehling gives figures varying from 46° to 58°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
10.6187	—0.0010	—0.0018	—0.002	—0.175	389.8	—68.20	—1061	23.5°
3.7933	—0.0024	—0.0028	—0.004	—0.047	389.6	—18.31	—797	22°

Average, —929 cals.

Ostwald quoting Berthelot would make the heat of solution 8.1 K on 810 cals. at 22°, the heat of solution decreasing with rising temperature.

Succinimide.

From Kahlbaum. Recrystallized from water and dried at 85°-100°. Small quantity of white fume given off at about 95°. Melting point = 124.5° cor. Beilstein gives 125°-126°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
5.5606	—0.0040	—0.0080	—0.024	—0.621	389.6	—242.0	—4306	21.5°
2.3592	—0.0026	—0.0024	—0.002	—0.262	389.5	—102.0	—4282	23.2°
						Average,	—4294 cals.	

Acetamide.

From Eimer and Amend. Distilled in ammonia and stirred while cooling to get small crystals. Seemed to be slightly moist though carefully protected from the air. Melting point = 73.3° cor. Beilstein gives 82°-83°. Fehling gives 78°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
5.1249	0.0000	—0.0006	—0.001	—0.439	389.6	—171.0	—1969	24.0°
2.7516	—0.0016	—0.0022	—0.002	—0.241	389.7	—93.90	—2014	23.0°
						Average,	—1991 cals.	

Ostwald, quoting Berthelot and André, gives 19 K or 1900 cals.

Mannite.

From Kahlbaum. Crystalline white. Was not further purified. Melting point = 165.5° cor. Beilstein gives 164°-166°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
4.5287	—0.0028	—0.0056	—0.011	—0.335	389.5	—130.5	—5245	22.5°
2.1767	—0.0004	—0.0010	—0.001	—0.162	389.8	—63.14	—5279	23.5°
						Average,	—5262 cals.	

Sugar.

Prepared from the purest rock candy obtainable. Only well developed crystals were kept. These were washed with water, dried, and powdered. Only a trace of glucose could be found.

6.3794	—0.0006	—0.0004	—0.001	—0.061	389.8	—23.73	—1275	23.0°
2.6436	+0.0004	+0.0002	—0.000	—0.027	189.4	—10.52	—1361	22.7°
						Average,	—1318 cals.	

Resorcinol.

From Kahlbaum. Crystallized. Was assumed to be pure. Melting point = 110.6° cor. Decomposed a little on melting. Beilstein gives melting point = 110° and 119°.

m.	Δt_1.	Δt_2	t.	ΔT.	M.	q.	Q.	T.
6.0850	—0.0020	—0.0030	—0.003	—0.564	389.6	—219.7	—3970	23.5°
3.0595	+0.0040	—0.00060	—0.001	—0.282	389.6	—109.8	—3950	22.5°
					Average,		—3960 cals.	

HEATS OF SOLUTION IN METHYL ALCOHOL.

Methyl alcohol from Kahlbaum. Labeled "Acetonfrei." Dehydrated with large excess of calcium oxide. After twenty-four hours distilled. Portion coming over at 64.3° cor. was used. Sp. gr. $\frac{15°}{4°} = 0.79619 = 99.9$ per cent. methyl alcohol by Landolt's and Bjornstein's tables. Mass of alcohol delivered between 20°–25° $= 373.9 \times 0.7870 = 294.3$ grams, or in water terms $= 294.3 \times 0.62 = 182.4$ grams water.

Urethane.

m.	Δt_1.	Δt_2	t.	ΔT.	M.	q.	Q.	T.
1.5032	—0.0032	—0.0068	—0.014	—0.369	—198.8	—73.36	—4346	24°

Acetanilid.

From Kahlbaum. Recrystallized from alcohol. Air dried. White. Slight, agreeable, aromatic odor. Melting point = 113.5° cor. Beilstein gives 112°; Fehling gives from 101°–113°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
2.1823	—0.0020	—0.0072	—0.018	—0.361	—198.8	—72.38	—4477	24.5°

Acenaphthene.

From Kahlbaum. White. Recrystallized from alcohol. Air dried. Melting point = 93.5° cor. Belistein gives 95° and 101°; Fehling gives over 100°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
1.4266	—0.072	—0.0082	—0.008	—0.288	198.8	—57.26	—6180	24°

Naphthalene.

From Kahlbaum. White. Recrystallized from alcohol. Air dried. Melting point = 80.1° cor. Beilstein gives 79.2° and 80.1°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
1.3594	—0.0018	—0.0038	—0.008	—0.226	198.8	—44.94	—4233	24°

HEATS OF SOLUTION IN ETHYL ALCOHOL.

Ethyl alcohol from Eimer and Amend and Chas. Cooper and Co. Marked absolute. Distilled, treated with calcium oxide, and redistilled. Boiling point, 77.6°–78.7° cor. Sp. gr. +0.7873. Mass of alcohol delivered between 20° and 25° = 373.9 × 0.7873 = 294.4 grams, or in water terms = 294.4 × 0.59 = 173.7 grams water.

Urethane.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.4826	−0.0010	−0.0084	−0.019	−0.976	190.3	−185.7	−4746	23.5°
2.5207	−0.0110	−0.0172	−0.017	−0.701	190.3	−133.4	−4710	23.8°
					Average,		−4728 cals.	

Acetanilid.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
2.8726	+0.0014	−0.0048	−0.009	−0.471	190.3	−89.74	−4212	−23°

Acenaphthene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.8306	+0.0038	−0.0046	−0.009	0.772	190.1	−146.7	−5899	25.0°
1.6855	−0.0014	−0.0024	−0.005	0.340	190.3	−64.71	−5614	23.6°
					Average,		−5906 cals.	

Naphthalene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
2.9976	−0.0036	−0.0104	−0.021	−0.599	190.1	−113.9	4861	24°

Urea.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
1.3715	+0.0003	−0.0046	−0.025	−0.434	190 1	−82.6	−3612	24°

Acetamide.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.4805	+0.0014	−0.0094	−0.019	−1.119	190.1	−212.7	−3606	23.3°

Phenanthrene.

From Kahlbaum. Crystallized three times from toluene. Air dried. Melting point = 100.4°. Beilstein gives 99°; Fehling gives 96° to 100°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
0.8259	−0.0008	−0.0022	−0.004	−0.105	190.3	−19.98	−4306	24°

Chloral Hydrate.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
8.0642	−0.0022	−0.0182	−0.018	−0.029	190.3	−5.519	−113.1	22°

Succinimide.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
4.1413	—0.0018	—0.0106	—0.043	—1.199	190.3	—228.2	—5456	21.5°

Benzamide.

From Kahlbaum. Recrystallized from water. Air dried. Melting point 126.0°. Beilstein gives 123°; Fehling gives 125°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
1.9457	—0.0018	—0.0052	—0.005	—0.361	190.3	—68.7	—4238	22.5°

Resorcinol.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
4.2003	—0.0016	—0.0016	—0.0024	+0.054	190.3	+10.28	+2692	22.5°

Toluidine (p).

From Kahlbaum. Very impure. Recrystallized from alcohol three times. Slightly yellowish, turned darker on exposure to air and light while drying. Air dried. Melting point 44.6°. Beilstein gives 45°.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.4900	—0.0018	—0.0074	—0.007	—0.623	190.3	—118.6	—3636	23.5°
1.3591	+0.0014	—0.0008	—0.001	—0.241	190.3	—45.87	—3665	24°
					Average,		—3650 cals.	

HEATS OF SOLUTION IN PROPYL ALCOHOL.

Propyl alcohol from Kahlbaum. Dehydrated with calcium oxide. Distilled. Distillate collected until an empyreumatic odor was observed. Sp. gr. $\frac{24°}{4°} = 0.80128$. Mass of alcohol delivered between 20° and 25° $= 373.9 \times 0.8013 = 299.5$ grams, or in water terms $= 299.5 \times 0.66 = 197.7$ grams water.

Urethane.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.3360	—0.0144	—0.0212	—0.021	—1.054	214.3	—225.9	—6045	24.7°

Acenaphthene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.0744	—0.0152	—0.0198	—0.040	—0.634	—214.3	135.9	—6807	13°

Naphthalene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
2.6408	—0.0112	—0.0158	—0.032	0.547	214.3	—117.2	--5681	23.0°

HEATS OF SOLUTION IN CHLOROFORM.

Chloroform from Eimer and Amend, Powers and Weightman,

and Charles Cooper and Co. Purified by washing with water till it gave no reaction for alcohol, drying with sulphuric acid or calcium chloride and distilling. No reaction for impurities with silver nitrate or potasssum hydroxide. Sp. gr. between 20° and 25° = 1.479. Mass of chloroform delivered = 373.9 × 1.479 = 553.0 grams, or in water terms = 553.0 × 0.2337 = 129.3 grams water.

Urethane.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.2930	+0.0014	—0.0082	—0.032	—1.161	145.7	—169.2	—4573	23.5°

Acetanilid.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
2.5859	+0.0026	—0.0038	—0.022	—0.584	145.7	—85.10	—4442	24.5°

Acenaphthene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
2.4138	+0.0008	—0.0072	—0.035	—0.482	145.7	—70.23	—4480	21°

Naphthalene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
0.9407	—0.0060	—0.0052	—0.005	—0.194	145.9	—28.31	—38.52	23°

Chloral Hydrate.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
7.0497	—0.0042	—0.0368	—0.137	—1.753	145.9	—255.7	—5993	21.7°

Toluidin (p).

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
1.2787	—0.0028	—0.0034	—0.011	—0.286	145.9	—41.74	—3492	23.3°

HEATS OF SOLUTION IN TOLUENE.

From Kahlbaum. Colorless. Redistilled. Boiling point 110.4°–110.7°. Sp. gr. between 20° and 25° = 0.8621. Mass of toluene delivered = 373.9 + 0.8621 = 322.3 grams, or in water terms = 322.3 × 0.3942 = 127.1 grams water.

Urethane.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
1.7615	—0.0002	—0.0100	—0.018	—0.881	143.7	—126.6	—6399	23°

Acenaphthene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
5.1897	—0.0066	—0.0202	—0.020	—1.115	143.9	—160.6	—4763	23°
1.6799	—0.0062	—0.0100	—0.010	—0.366	143.5	—52.51	—4818	23°
						Average,	—4788 cals.	

Napthalene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
2.3937	—0.0010	—0.0074	—0.007	—0.550	143.9	—79.13	—4332	23°
0.9916	—0.0034	—0.0064	—0.013	—0.232	143.9	—33.34	—4302	23°
					Average,		—4267 cals.	

Chloral Hydrate.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
2.8739	—0.0090	—0.0156	—0.056	—0.913	143.5	—131.0	—7537	24°

Phenanthrene.

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.6075	—0.0046	—0.0076	—0.015	—0.504	153.7	—72.71	—3588	24.7°
1.3179	—0.0084	—0.0108	—0.011	—0.179	143.5	—25.69	—3469	23°
					Average,		—3528 cals.	

Toluidine (p).

m.	Δt_1.	Δt_2.	t.	ΔT.	M.	q.	Q.	T.
3.8683	—0.0080	—0.0189	—0.019	—1.247	143.7	—179.2	—4956	24.7°
1.9525	+0.0024	—0.0032	—0.003	—0.636	143.7	—91.40	—5011	23°
					Average,		—4983 cals.	

The quantity of solvent compared with the quantity of substances dissolved is so large that it is safe to conclude that further addition of solvent would produce no appreciable evolution of heat. Besides, it is plain from the above experiments that in many cases a difference of 100 per cent. in the quantity of solvent produced no decided change.

The following table shows the heats of solution in a convenient form for comparison.

	Water.	Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	Chloroform.	Toluene
Urea	—3628	......	—3612	......	......	......
Urethane	—3787	—4345	—4728	—6045	—4573	—6399
Chloral hydrate	—929	......	—1131	......	—5993	—7537
Succinimide	—4294	......	—5456	......	......	......
Acetamide	—1991	......	—3606	......	......	......
Mannite	—5262	......	......	......	......	......
Resorcin	—3960	......	+269.2	......	......	......
Benzamide	......	......	—4238	......	......	......
Toluidine (p)	......	......	—3650	......	—3492	—4983
Acetanilide	......	—4477	—4212	......	—4442	......
Acenaphthene	......	—6180	—5986	—6807	—4480	—4788
Naphthalene	......	—4233	—4861	—5681	—3852	—4267
Phenanthrene	......	......	—4306	......	......	—3528
Sugar	—1318	......	......	......	......	......

RUTGERS COLLEGE, October 12, 1895.

A STUDY ON SOME GAS-PRODUCING BACTERIA.

By A. A. Bennett and E. E. Pammel.

Received November 29, 1895.

THE manifold interests connected with micro-organisms, because of their causal relations to certain diseases of man and also of the lower animals, and the part they play in many important economic problems have stimulated much investigation by physicians and biologists. The field is, however, very great and the explorations have just begun.

There are many questions connected with this subject that are yet unsettled and many that have not as yet been touched upon. The physician in studying micro-organisms has always before him the consideration of their relation to the disease in question. Other phases of the life of these germs are not at all considered by these investigators, thus leaving the important questions of classification, physiology and the chemistry of their life and development to the botanist and chemist. The purpose of this paper is to make a small contribution to a phrase of the chemical side of this question, namely, to a study of the gases produced during the development and growth of some micro-organisms.

Although the study of the products of chemical decompostion formed by micro-organisms has not been very extensive or very thorough, yet much has been learned in a qualitative way. The substances produced by bacteria are quite numerous, including solids, liquids and gases. The same products are often produced by different organisms in varying proportions.

Among the solids produced are the ptomaines, indol, skatol, leucine, tryrosine, succinic and malic acids, etc. The liquid products include alcohol, acetic and lactic acids. The gases formed are quite numerous and include hydrogen sulphide, ammonia, carbon dioxide, hydrogen and methane. In cases in which ammonia and hydrogen sulphide are produced simultaneously, they unite and form ammonium sulphide.

The importance of the study of these compounds, both qualitatively and quantitatively, is evident when the character of such products as are included under the general term ptomaines and leucomaines, also tuberculin, antitoxine, etc., are considered

ered. A knowledge of the gaseous products and the conditions under which they are formed is often of great service to the biologist in identifying different species. This is well illustrated by a condensed statement taken from an article by Dr. McWeeney in "Modern Medicine and Bacteriological Review," Vol. 3, August, 1894.

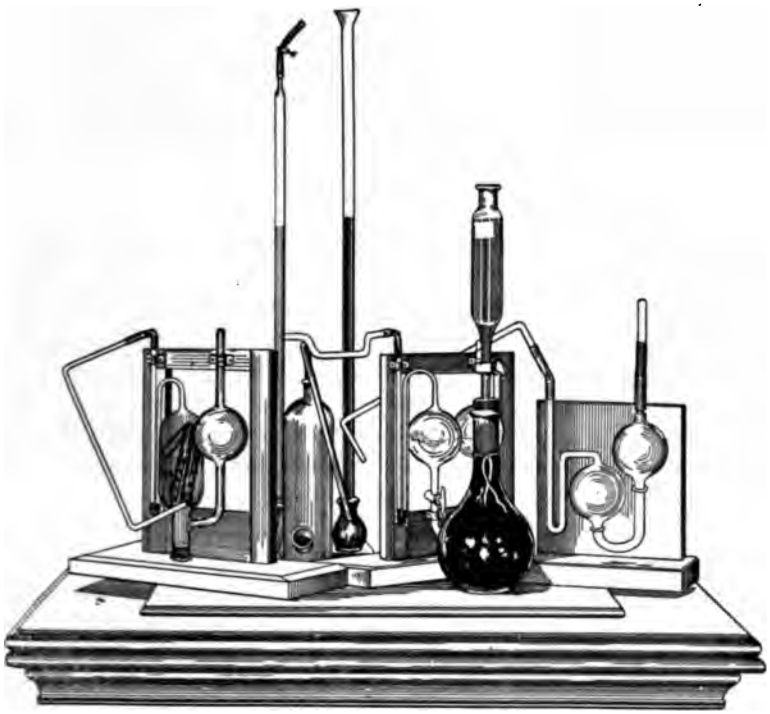
Dr. McWeeney says in this article that he made a study of the microbic cause of an epidemic of typhoid fever, which had recently occurred in the village of Waterford, England, using the method of Pariettis, Globis, and others. He identified the microbes as those of Eberths (that causing typhoid fever), while the fermentation test of Dr. Theobald Smith, of Washington, indicated on the contrary that the bacillus was not that of Eberth, but was the bacillus coli, since it produced decomposition of lactose, although not quite so freely as another specimen of bacillus coli with which it is compared. The bacillus of Eberth's did not, however, produce decomposition of lactose as does the bacillus coli.

It is a well known fact that micro-organisms, when surrounded by the conditions favorable to their growth, namely, a proper food supply, moisture, favorable atmospheric conditions, and temperature, develop very rapidly for a time. However, after a certain period the rate of development diminishes until finally it ceases entirely, although there may be a large supply of food material still unused and the general conditions have not changed. For example, the saccharomyces produces alcohol from sugar until about fifteen per cent. of the media becomes alcohol, when action practically ceases. A twenty per cent. solution of alcohol is antiseptic. Many illustrations for the effect on the growth of bacterial forms might be adduced, but they are too familiar facts to be repeated here.

In a study made by the authors an attempt was made to accurately estimate the constituents of the mixed gaseous products by a variety of bacteria. Hempel's apparatus was used for the estimation of the gases. The pieces employed are shown in the cut that accompanies this article.[1] The culture flask is the only apparatus that needs description. It consists of a half liter flask

[1] See Hempel's "Gas Analysis" for description.

closed with a three-holed rubber stopper, through one of the openings of which is passed the stem of a 100 cc. separatory funnel until it nearly reaches the bottom of the flask. Into the



second opening is inserted a fine capillary tube, bent at right angles, which serves to conduct the gas to the mercury gasometer. The third opening serves for the thermometer when temperature determinations are made. The flask is connected with the mercury gas-holder when ready for the connection of the gases.

The separatory funnel was used for inoculating the medium. The method of procedure is as follows: The tank is filled nearly full of the food medium which had been properly sterilized. The separatory funnel, which was filled about two-thirds full of the sterilized medium, was now inserted and the whole resterilized.

The stopper was next crowded in and the stop-cock opened. The medium in the funnel was allowed to run into and fill the small vacant space below the stopper and force the liquid through the capillary tube until the latter is filled over to the mercury. The stopcock was then closed and the apparatus was ready for the collection of the gases. From the gas-holder the gas was transferred to the burette and the analysis carried on in the usual manner, except that mercury was used in the burettes instead of water.

PREPARATION OF THE MEDIA.

The fluid in all cases was peptone bouillon containing either glucose, lactose, or cane sugar. The bouillon was prepared by using either 250 grams of finely chopped lean beef, or five grams of Liebig's extract. After the meat was thoroughly cooked it was filtered, and to the filtrate was added five grams of salt, twenty grams of sugar and ten grams of dried peptone. It was then made up to a liter. The medium was now put in a flask and separatory funnel as before directed and sterilized for three successive days in a Kock's steam sterilizer, when it was ready for use. The Liebig's extract was treated in the same manner as was the meat extract.

The bacteria in all cases were taken from fresh cultures, grown either upon agar-agar, gelatin or potato. The medium in which the bacteria grew was in all cases neutral.

The following are the tabulated results of a few of the gas-producing organisms of which a study was made :

TABLE No. I.—BACILLUS AROMATICA.

	Temp.	Date.	Kind of sugar:	Gas present after days. 1	2	3	4	5	No. cc. taken.	Carbon dioxide. Per cent.	Hydrogen. Per cent.
1.	28°	July 23	Glucose.	0	87.5	173.	237.0	....	38.4	26.04	73.9
	18°	Oct. 1	Glucose.	0	...	...	...	45.4	15.7	26.68	73.3
2.	28°	Aug. 2	Cane....	0	39.5	..	93.8	122.9	18.7	23.5	76.4
	24°	Aug. 17	Cane....	0	...	...	...	....	32.2	21.8	78.0
3.		Aug. 10	Lactose.	0	0	0	0	0	0	0	0
		Aug. 15	Lactose.	0	0	0	0	0	0	0	0

TABLE NO. II.—MICROCOCCUS FROM CHEESE.

Date.	Kind of sugar.	Gas present after days. 1	2	3	4	5	No. cc. taken	Carbon dioxide. Per cent.	Hydrogen. Per cent.
July 29	Glucose....	0	0	0	0	0	0	0	0
Sept. 22	Glucose....	0	0	0	0	0	0	0	0
Aug 2	Cane.......	0	0	0	0	0	0	0	0
Sept. 22	Cane.......	0	0	0	0	0	0	0	0
Aug. 20	Lactose	0	0	0	0	0	0	0	0
Sept. 15	Lactose	0	0	0	0	0	0	0	0

TABLE NO. III.—JONES ANAEROBE.

Temp.	Date.	Kind of sugar	Gas present after days. 1	2	3	4	5	No. cc. taken	Carbon dioxide. Per cent.	Hydrogen. Per cent.
1. 28°	Sept. 6	Glucose..	76.6	134.6	....	...	..	24.3	27.8	72.1
	July 23	Glucose..	...	....	....	...	..	72.0	11.5	82.4
2.	Aug. 29	Cane	0	136.8	151.8	...	..	...	42.3	57.6
	July 8	Cane	...	....	....	...	..	85.0	44.7	55.3
3.	Aug. 6	Lactose..	0	0	0	0	..	0	0	0
	Sept. 15	Lactose..	0	0	0	0	..	0	0	0

TABLE NO. IV.—BACILLIS COLI COMMUNIS.

Temp.	Date.	Kind of sugar.	Gas present after days. 1	2	3	4	5	No. cc. taken.	Carbon dioxide. Per cent.	Hydrogen. Per cent.
1. 28°	Sept. 6	Glucose..	119.6	162.0	....	...	0	31.0	25.16	74.8
22°	Sept. 30	Glucose..	....	76.6	....	...	...	45.0	23.2	76.8
2. 24°	Aug. 17	Cane	0	7.5	34.0	40.1	0	37.0	34.3	65.4
22°	Oct. 15	Cane	0	....	....	5.2	...	28.0	31.6	68.4
3. 26°	Aug. 27	Lactose ..	0	....	....	76.6	233.5	27.0	28.8	71.1
	Oct. 19	Lactose ..	0	....	140.1	...	...	35.3	27.2	72.8

TABLE NO. V.—BACILLUS COLI COMMUNIS.[1]

Kind of sugar.	Per cent. of gas present after days. 1	2	3	4	5	6	7	Total gas at 20°–25°.	Reaction of bulb.	Carbon dioxide. Per cent.	Hydrogen. Per cent.
Glucose	28.0	44.0	47.0	..	..	..	..	9 days. 44.	......	32.0	68.0
Cane	..	31.0	..	47.0	..	50.0	..	11 days. 43.	Acid.	36.5	63.5
Cane	..	7.0	..	13.0	..	15.0	16.0	10 days. 19.	Alkali.	23.0	77.0
Lactose	28.0	42.0	45.0	48.0	..	52.0	..	45.0	......	37.0	35.0

[1] This table taken from Dr. Theobald Smith's work.

TABLE NO. VI.—BACILLUS MESENTERICUS VULGATUS.

Temp.	Date.	Kind of sugar.	Gas present after days. 1	2	3	4	5	6	No. cc. taken	Carbon dioxide. Per cent.	Hy-dro-gen. Per cent.
22° C.	Oct. 2	Glucose.	0	0	0	0	0	0	0	0	0
24° C.	Oct. 7	Glucose.	0	0	0	0	0	0	0	0	0
25° C.	Sept. 15	Cane ...	0	76.6	99.6	166.90	...	0	32.2	61.1	38.8
22° C.	Oct. 15	Cane ...	.	...	76.6	......	...	.	32.0	63.7	36.3
	Sept. 22	Lactose.	0	...	...	79.1	96.	.	22.8	23.5	76.5

A bacillus from butter-milk, not yet named, was used to inoculate a glucose peptone medium. The results being negative so far as gas development goes they are not tabulated. Action began in the separatory funnel, in course of twenty-four hours, and gas was quite rapidly developed. No gas was found in the flask after standing for four days and until action had ceased in the funnel. An examination of the medium in the flask showed that it was very markedly acid, showing that decomposition had taken place. The result is of value only as it shows that this bacillus can develop in the same medium with or without air and that the products vary in kind and amount.

STATEMENTS AND OBSERVATIONS ON THE TABULATED RESULTS.

1. As before mentioned, the media were neutral in all cases and were peptone bouillon, to which were added the different sugars, as noted in the tables.

2. The gas should not be analyzed until the action is about complete, owing to the fact of absorption of the carbon dioxide by the media. The first portions of the escaping gas were in the cases examined nearly pure hydrogen. Therefore in considering the total gaseous products the absorbed carbon dioxide should be taken into account. It was found that each cc. of the media absorbed on the average at ordinary temperatures eight cc. of carbon dioxide.

3. The temperature of the media has a marked effect, as is well known, on the rapidity and the time necessary for the development of the gas.

A difference of ten degrees made a difference of four days in the time of completing the action in the case of bacillus aromaticus.

4. It will be noticed that at the same temperature the action starts at different periods and that the maximum action occurs at different lengths of time from the time of inoculation.

5. Alcohol was produced by several of the bacteria studied. Bacillus aromaticus produced no alcohol, but did form lactic acid. The micrococcus from cheese produced no gas in any case, *i. e.*, not enough to more than saturate the media, although there was evidence of quite active growth.

6. The solutions were acid in all cases at the end of the action. Lactic acid was found in most cases.

7. Jones' anaerobe produced acetic and lactic acids with glucose, lactic acid, and only a trace of acetic acid with cane sugar. The alcohol was more abundant in the latter case.

8. Bacillus coli communis produced no alcohol, but did form lactic acid.

9. The bacillus mesentericus vulgatus rendered the media but slightly acid. No alcohol was produced.

10. It should be noted that the amount of carbon dioxide produced by the different micro-organisms studied varies with the kind of sugar used. See Table VI in reference to glucose and lactose. This evidently shows a smaller capacity to procure oxygen in one case than in the other.

11. Looking at the tabulated results under bacillus aromaticus, it will be seen that the organism produces gas in solutions of glucose and cane sugar, but it does not produce any gas in solutions of lactose sugar.

12. In comparing the total amounts of gases produced by different species of bacteria, it is seen that they are the most active in glucose media, with the exception of bucillus mesentericus vulgatus, which produces no gas in glucose media. This fact will serve to distinguish this bacillus from a larger number of others.

13. Bacillus aromaticus and Jones' anaerobe produce gas in solutions of glucose and cane sugar, but none in lactose sugar. Coli communis on the other hand produces gas in solutions of all three sugars, the largest amount of gas being produced in the lactose solution.

Where no record of gas production is made in the tables it

means that action practically ceased before this time was reached.

SOME OF THE INVESTIGATIONS, PRINCIPALLY OF GASEOUS PRODUCTS, OF THE GROWTH OF MICRO-ORGANISMS ARE SUMMARIZED HERE.

The following interesting conclusions from a study of stomach dilatation are drawn by Hoppe-Seyler:

First. In not a few cases (thirteen out of twenty-two) there were present carbon dioxide and hydrogen.

Second. The formation of hydrogen depends on butyric ferment.

Third. The formation of this hydrogen goes on even when the fluid contents of the stomach reaches two per cent. of sodium chloride.

Fourth. By removal of sodium chloride there is usually a larger per cent. of carbon dioxide.

Fifth. By the yeast ferment carbon dioxide only is formed.

Sixth. Often the dilated stomach only contains the gases that have been swallowed.

Another very important investigation of the products of bacterial decomposition was made by Brieger, using the pneumococcus of Friedländer.

By growing this specific germ in suitable solution of grape or cane sugar, he obtained principally acetic, together with some formic and succinic acids and ethyl alcohol. The same products were also obtained by the growth of this organism in solution of calcium lactate and creatine. In bacillus ethaceticus the amount of alcohol and acetic acid stand to each other in virtually the same proportions as does that produced by bacillus pneumococcus, yet the absolute amounts produced are much less than in that of the latter.

There is often some difference in the day when fermentation begins, but Frankland, Stanley and Frew remark that (although there is some difference in the several series of experiments as to the precise period which elapses between the time of inoculation and the commencement of fermentation) the balance of evidence points to the glucose being the least, and to the mannitol and cane sugar being the most fermentable. In the glucose fer-

mentation of pneumococcus the proportion of hydrogen to carbon dioxide by volume shows that the gases are given off in approximately the same number of molecules of each, but when mannitol was used ten molecules of hydrogen to twelve molecules of carbon dioxide were produced. This larger proportional evolution of hydrogen in the case of mannitol is what might have been anticipated from a consideration of the larger per cent. of hydrogen in mannitol.

Gartner also made some very interesting investigations. He studied mainly one bacterium, which he called a new gas-producing pathogenic bacillus. He inoculated different media containing varying quantities of sugar and peptone, also media showing different reactions. Different products and different proportions of products were obtained in most cases. He states that a three per cent. glucose medium gives a relatively larger per cent. of gas than a one and one-half per cent. solution ; also that an acid reaction hinders the production of gas and the total amount of gas is not as much as was formed from the same solution when it was neutral.

Another investigator of the gases produced by bacteria deserves mention, namely, Dr. Theobald Smith, of Washington.

Dr. Smith, in his analysis, used a fermentation tube devised by himself. The media and fermentation tubes were completely sterilized, after which the media was inoculated with specific germs. The gas was afterwards determined by using potassium hydroxide as an absorbing material for the carbon dioxide. The remainder of the gas he calls an explosive gas and assumes it to be hydrogen.

The types of bacteria which he took were bacillus coli communis, hog cholera bacillus, B. lactis aerogenes, bacillus of Friedlander, B. aedematis maligni, proteus vulgaris, B. cloacea and saccharomyces.

The result of his study of these micro-organisms was to show that the media conditions under which development took place modified the proportion of the gaseous products and the rapidity of their formation. His results also show that these facts may be used to a marked extent to determine species.

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CHEMICAL VS. BACTERIOLOGICAL EXAMINATION OF POTABLE WATER.[1]

W. P. MASON.

Received November 16, 1895.

APROPOS of the recent articles upon this question, which have appeared in the English papers, it is noteworthy that there is a growing tendency among physician and civil engineers to belittle the chemis's opinion regarding the potability of a water, and to pin their faith exclusively upon what the bacteriologist may have to say upon the subject. This feeling is strengthened by the publication of the results of such trials as that undertaken by the London Local Government Board, in which it will be remembered, water samples purposely inoculated with typhoid germs, were sent for analysis to one of England's leading chemist and were by him pronounced pure.

Those who set special value upon such a "test" of methods as the above, and who consider it quite final as showing the

[1] Read before the New York Section.

inability of chemistry to detect pollution in a liquid which the bacteriologist would instantly pronounce very foul, should remember that such a sample of water could not be found in practice, and that the very conditions under which it was prepared, eliminated the chemical items indicating pollution, while it increased tremendously the signs governing the bacteriological side of the case.

The bacteriologist sought for the Eberth bacillus, and very naturally, quickly found it in a water purposely sown with a culture of the germ.

The chemist looked for those elements which always occur in sewage-laden water, whether the sewage be from sources of disease or otherwise, and, not finding them, he pronounced the water to be what it really was, free from sewage addition.

Sewage, as it occurs in practice, contains an immense deal of material other than that productive of disease, and it is upon just this comparatively harmless, but constantly present material that the chemist relies for the indication upon which he bases his opinions.

He is unable to say whether or not a sewage-laden water is disease-bearing on any particular date, for to him all sewage is alike, but he condemns the water, for the reason that, although it may be harmless to-day, it is impossible to predict what may be its condition to-morrow.

Within the week, I have been requested to make a bacteriological examination of the water of a certain well, in order to determine if it be effected by neighboring cesspools.

The physician who made the request was impressed with belief in the paramount value of such an examination and the comparative uselessness of chemical analysis.

I am quite convinced that, had I followed his suggestion, I should have sought in vain for any specific microbe, but inasmuch as upon chemical analysis, I found that the "chlorine" ran twenty-four parts per million, which is about ten times the local "normal," and the "nitric nitrogen" read nine parts per million in place of 0.116, I condemned the water off hand without going further.

There is simply no comparison between the two methods in

question for water problems of this class, and the value of chemistry is still more pronounced in those instances where it is possible to introduce common salt or lithium chloride into a source of suspected pollution, and then look for increased chlorine or presence of lithium in the water of the well. In legal cases touching upon this point of contamination of wells, by cemeteries for instance, the chemical testimony is especially strong.

In the matter of determining the suitability of a stream for city supply, the services of the bacteriologist should be unquestionably secured, but it is doubtful if his report can be considered of more importance than that of the chemist.

Chemical analysis, by comparing the water taken at the site of the proposed intake with that from the same stream above all points of possible pollution, can indicate whether or not up stream contamination is felt at the lower point; nor is it necessary that the polluting sewage be from pathogenic sources in order that its presence may be recognized.

As Dr. Dupré has pointed out, chemistry in such cases anticipates what may happen in the future, and, by timely advice, may prevent an outbreak of disease, while, on the other hand, the discovery of disease germs in a water is only possible after the water has become infected.

Bacteriology is of especial value, and greatly superior to chemistry, for the testing of filters and watching any variation in their efficiency.

For this purpose the simple count of germs per cc. is most valuable, and differentiation is a secondary matter; for the assumption is a just one, that a filter which will remove the harmless bacteria, will take out the objectionable ones as well.

It is very far from my desire to decry the value of bacteriology, but I cannot but feel, that in their enthusiasm over the great triumphs of the new science, the people at large have gone slightly "bacteria mad," and are apt to expect more than can be furnished by the means and information now available.

RENSSELAER POLYTECHNIC INSTITUTE, TROY, N. Y.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. No. 9.]

THE ELECTROLYTIC ESTIMATION OF MERCURY.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

Received November 29, 1895

THE precipitation of this metal from a cyanide solution[1] has given quantitative results, which render the electrolytic procedure decidedly more advantageous to the analyst than the usual gravimetric course. However, conditions sometimes occur when even the preceding rapid method is made time-consuming. Thus in the working with mercury sulphide it would be necessary to first dissolve the substance in acids and remove the excess of the latter before advancing to the electrolytic decomposition of the resulting salt. Conscious of this fact and that mercury sulphide, as cinnabar, is a natural product, which is quite often offered for analysis, we took occasion to review the method first proposed by Smith,[2] and subsequently confirmed by Vortmann,[3] *viz.*, the electrolytic deposition of mercury from its solution in an alkaline sulphide. The chief point to be ascertained was whether the time factor could be reduced. This had been accomplished with the cyanide solution by simply applying a gentle heat, thereby precipitating two-tenths gram of metal in about two hours. Another point which we wished to definitely establish was the exact current density for a given electrode surface. To this end several determinations were made, using a mercuric chloride solution of known mercury content:

Mercury present as chloride. gram.	Mercury found. gram.	N. D. of Current in amperes for 100 sq. cm. surface.	Dilution of solution. cc.	Time.	Temp.
0.1913	0.1917	0.13	125	3 hrs.	65°
"	0.1916	"	"	"	"
"	0.1908	"	"	"	"

In each case twenty cc. of sodium sulphide of specific gravity 1.22 were present.

These results indicate that mercury can be determined as rapidly and as accurately in this way as when working with a cyanide solution.

[1] This Journal, 17, 612.
[2] *J. Franklin Inst.*, 1891 and *J. Anal. Chem.*, 5, 202.
[3] *Ber. d. Chem Ges.*, 24, 2749.

We next determined the mercury in a sample of cinnabar by distilling the latter with lime, collecting and weighing the metal as directed in Fresenius' Quantitative Analysis, Am. Ed., p. 306.

1. 0.9590 gram of mineral gave 0.8194 gram of metal, or 85.44 per cent.

2. 0.8586 gram of mineral gave 0.7325 gram of mercury, or 85.31 per cent.

Portions of the same mineral were weighed out in platinum dishes and after solution in twenty to twenty-five cc. of sodium sulphide of specific gravity previously mentioned, were diluted with water to 125 cc. and electrolyzed at a temperature of 70°, with a current of $N.D._{100} = 0.12$ ampere. The period of time allowed for the precipitations never exceeded three hours. The results were:

	Cinnabar. gram.	Mercury. gram.	Percentage.
1	0.2167	0.1850	85.37
2	0.2074	0.1769	85.29
3	0.2432	0.2077	85.40

We would observe that during the electrolytic decomposition the platinum dishes should be carefully covered to prevent evaporation, thereby exposing a rim of metal, which if not in part volatilized, would yet be changed to mercury sulphide. The latter is indicated by a dark-colored film. With a little attention there should be no question as to the final outcome of any determination made in this way. We regard the method as entirely satisfactory. The short time required for a determination, as outlined above, will recommend it in our judgment to analysts generally.

UNIVERSITY OF PENNSYLVANIA.

THE PRECIPITATION OF PHOSPHOMOLYBDATE IN STEEL ANALYSIS.

BY GEORGE AUCHY.

Received December 2, 1895.

IN a recent paper[1] Messrs. Blair and Whitfield give a new formula for the preparation of molybdate solution, which is a great improvement on the old one, as by its use the seperation of

[1] This Journal, 17, 747.

ammonium molybdate from the solution by long standing is avoided and the solution retains its strength. In using solution of the new formula, however, the writer, a number of times, has had a further precipitation of phosphomolybdate to occur after filtration. This additional precipitate could not have resulted from insufficiency of molybdate solution—sixty to seventy-five cc. of the solution having been used; nor from insufficient shaking—ten minutes having been given in each case. The precipitation seemed to be the result of the dilution of the liquid by the wash water, and not of the longer standing, as in several cases the original phosphomolybdate precipitate had stood an hour or more, and in one case, all night before filtering. This seemed an indication that dilute solution is a help to complete precipitation. But the query then arose, Why had this after separation of phosphomolybdate never occurred before in using molybdate solution of the old formula? The explanation at once suggested itself. Because when solution of the old formula is used the amount of ammonium nitrate present is necessarily much larger. If these assumptions are correct, it then would seem then that the presence of ammonium nitrate and a dilute solution are both important factors in the thorough precipitation of the phosphomolybdate (the former is, indeed, a well known fact). Acting upon this hint, precipitations have since than taken place in solutions of larger volume, and containing a greater proportion of ammonium nitrate; effected by increasing the volume of nitric acid (sp. gr. 1.13, recommended by Drown), as used for solution of two grams steel, to 100 cc., and the amount of strong ammonia used for neutralization, to fifteen cc. diluted with fifty cc. cold water. The following few experiments which the writer has had time to make, give some corroboration to this theory.

Experiment 1. Heat 369. 1. Solution nearly neutral. Volume small. Considerable ammonium nitrate present. Sixty cc. nitric acid (1.13) for solution of the steel. Eight cc. strong ammonia for neutralization. Thirty-five cc. molybdate solution of old formula, —0.009 per cent.

2. Solution very strongly acid. Dilute in volume. Large excess of ammonium nitrate present. One hundred cc. nitric acid (1.13) for solution. Fifteen cc. strong ammonia for neu-

tralization. Then fifty cc. strong nitric acid, and fifteen to twenty grams of crystallized ammonium nitrate. Sixty cc. of molybdate, new formula, —0.010 per cent.

Experiment 2. Heat 352. 1. Solution nearly neutral. Volume dilute. Considerable ammonium nitrate present. One hundred cc. nitric acid (1.13) for solution. Fifteen cc. strong ammonia for neutralization. Sixty cc. molybdate solution of new formula, —0.161 per cent.

2. Solution very strongly acid. Volume dilute. Large excess of ammonium nitrate present. One hundred cc. nitric acid (1.13) for solution. Fifteen cc. strong ammonia for neutralization. Then fifty cc. strong nitric acid, and fifteen to twenty grams of crystallized ammonium nitrate. Sixty cc. molybdate solution of new formula, —0.160 per cent.

These results tend to show that rather large dilution and plenty of ammonium nitrate are important conditions in the complete precipitation of the phosphomolybdate, and that the degree of neutralization of the nitric acid before precipitation is unimportant, the complete precipitation depending, not upon the approximate neutralization of the liquid, but upon the amount of ammonium nitrate present and the dilution of the solution. The reverse of this (solution small in bulk and nearly neutral) is sometimes recommended.[1] As before stated, about the right dilution and the proper amount of ammonium nitrate seems to be obtained by using one hundred cc. nitric acid of specific gravity 1.13 for solution of the steel, and fifteen cc. strong ammonia in fifty cc. cold water for neutralization previous to the addition of the molybdate solution. But if it be desired to have the solution less in volume, this amount of ammonium nitrate will not always suffice, as the writer has found by experience. The dilution seems to be an important requisite when molybdate of the new formula is used.

The amount of phosphorus precipitating after filtration, in the cases referred to (determined as pyrophosphate to guard against the contingency of the separation being ammonium molybdate merely), was respectively 0.026, 0.003, and 0.013 per cent.

As showing the very great degree of error that may occur

[1] This Journal, 17, 131.

from the careless use of molybdate solution of the old formula, the following results may be of interest to members of the society.

The molybdate solution had been made up for two—possibly three or four weeks. Then a close-down of the works for three weeks for repairs, at the end of which time the use of the solution was thoughtlessly resumed. But the extreme lowness of the results for heats 307 and 308 threw suspicion upon the solution, and duplicate determinations were made with fresh solution and continued till complete demonstration was had that the molybdate solution was at fault.

	With old solution. Per cent.	With fresh solution. Per cent.
Heat 306	0.048	0.060
" 307	0.004	0.006
" 308	0.002	0.006
" 309	0.033	0.035
" 310	0.013	0.020
" 311	0.002	0.007
" 312	0.002	0.006
" 313	0.001	0.008
" 314	0.012	0.036
" 315	0.010	0.049
" 316	0.001	0.007
" 317	0.008	0.049
" 318	0.002	0.020

Many authorities advocate the taking of the temperature of the liquid before the addition of the molybdate solution ; or the precipitation of the phosphomolybdate at a certain exact temperature—85° usually. The writer ventures to question whether, in a busy iron or steel works laboratory, it is worth while to take this trouble. For if five minutes be allowed for cooling after the solution is withdrawn from the flame, or if the flask be plunged into cold water a couple of times, there is no danger of its temperature being over 85° ; and Babbitt has shown that down to 25° all the phosphorus precipitates. Doolittle habitually precipitates at 35° to evade arsenic. Another authority (Johnson, I think) avoids a temperature higher than 50° to prevent oxides of iron and alumina from precipitating with the phosphomolybdate. So that where arsenic is not present any temperature

between the wide limits of 25° and 85° is all right, and one can not err in omitting the use of the thermometer altogether. The iron is not likely to precipitate if the solution be acid enough. Nevertheless a temperature below 50° is perhaps better than one higher.

As a reducing agent, perhaps the majority of chemists follow Jones in favoring ferrous sulphate. The writer found considerable phosphorus[1] in a lot of nice clean looking sulphate labelled "Free from phosphorus," and has since then used sugar as originally recommended by Dr. Drown. The queerest experience in the way of impure chemicals was the finding of phosphorus in "C. P" nitric acid—enough to add 0.06 per cent. to the real percentage in the steel. A second bottle from the same makers also contained it, though not in so great amount.

THE USE OF THE CALORIMETER IN DETECTING ADULTERATIONS OF BUTTER AND LARD.[2]

By E. A. de Schweinitz and James A. Emery.

Received January 3, 1896.

WHILE engaged in a study of the comparative value of butters and oleomargarines, it occurred to one of us that possibly the determinations of their respective heats of combustion might be useful if taken in connection with other data. Prof. Atwater, who has for some time been conducting experiments with an improved calorimeter, very kindly consented to burn such samples as might be sent to him. The first results were so interesting that it occurred to us at once that this method might be useful in detecting the adulteration of butter with oleomargarine, and also perhaps in distinguishing between lards of different sources and compound lards. Accordingly, some especially selected samples of which duplicates were kept in our laboratory, were sent to Prof. Atwater, and in the case of the butters and oleomargarines the results confirmed our first suppositions. In the use of the lards, however, the results were not so sharply distinctive, but taken in conjunction with other analytical data will prove, as we will endeavor to show,

1 Not enough, however, to affect the results very seriously. 0.111 per cent. instead of 0.105 per cent., for instance; and 0.056 and 0.054 per cent. in another steel.

2 Read at the Cleveland meeting, Dec. 31, 1895.

TABLE I.

Analyses of Butters and Oleomargarines.

No.	Manufacturer.	Specific gravity at 100° C.	Water. Per cent.	Vol. $\frac{n}{10}$ $Ba(OH)_2$ for 2.5 grams.	Salt. Per cent.	Casein. Per cent.	Ash. per cent.	Melting point. °C.	Iodine equivalent.	Combustion calories per gram. Atwater.	Cottonseed oil Bechi's test.	Coloring matter.	Sample No.
1	Oakdale M'f'g Co., oleomargarine	0.8916	8.09	0.30	4.02	1.46	4.24		62.19		No reaction		1
2	" " " "	0.8638	9.68	0.17		1.43	4.68		63.52				2
3	Vermont " " "	0.8667	10.96	0.25	6.60	1.56	6.01		66.69				3
4	" " " "	0.8913	9.32	0.15	4.80	0.07			61.44				4
5	Woodlawn Dairy Co., "	0 8848	9.40	0.17	5.40	4.83		25.0°	62.83				5
6	" " " "	0.8911	9.86	0.20	6.80	0.48		25.0°	63.26				6
1	Oakdale M'f'g Co., "	0.8840	9.81	0.42	3.52	1.44	3.38	22.5°	60.62		No reaction		7
2	Vermont " " "	0.8808	8.52	0.55	4.43	1.41	4.77	24.0°	59.11		Slightly dark		8
3	Oakdale M'f'g Co., "	0.8835	8.53	0.42	5.17	1.36	5.95	23.0°	52.80	9.599	Purple brown		9
4	" " " "	0.8865	10.69	0.27	2.99	1.21	2.96	25.0°	60.05		No reaction	Highly color'd	10
5	" " " "	0.8834	7.37	0.35		1.16	5.29	24.5°	63.12		Purple brown		11
6	" " " "	0.8906	8.00	0.35	3.75	2.59		25.0°	54.49	9.620	" "		12
7	" " " "	0.8914	6.86	0.42	3.42	1.77		22.5°	58.57		No reaction	Highly color'd	13
8	Vermont " " "	0.8828	9.47	0.35	5.31	1.35	5.67	25.0°	66.50	9.795	Purple brown		14
9	" " " "	0.8857	9.73	0.45	4.36	1.53	4.49	21.5°	68.03		No reaction	Highly color'd	15
10	" " " "	0.8874	9.00	0.30	3.68	1.66	3.68	22.5°	66.59	9.649	Purple brown		16
11	Woodlawn " " "	0.8992	9.23	0.35	3.97	1.47	3.78	22.0°	61.44		Slight dark'ng		17
	Swift & Co., "	0.8830	8.32	0.22	2.12	0.81	2.19	24.0°	60.67	9.644	No change	Highly color'd	18
	Hammond, "	0.8891	9.15	0.22	6.69	1.43	6.21	25.0°	60.53	9.607	" "	V'y high'yc'l'd	19
	Brown, Fitzgerald & Co., "	0.8876	9.25	0.27	4.04	0.77	4.00	26.5°	53.37	9.574	" "		20
1	Woodlawn Dairy Co , "	0.8818	9.87	0.82	5.22	2.64	5.70	25.5°	58.12	9.613	" "		21
2	" " " "	0.8880	9.23	0.35	3.80	1.52	3.68	22.5°	61.80	9.670	No reaction	Highly color'd	22
3	" " " "	0.8883	10.68	0.22	5.63	1.53	5.18	22.0°	65.73				23
4	" " " "	0.8943	7.91	0.22	3.17	1.13	3.24	23.0°	65.24				24
5	Goshen M'f'g Co., "	0.8998	9.37	0.22	5.82	1.63	5.42	23.5°	64.66	9.615	No reaction		25
	Elgin creamery, butter	0.8925	8.32	11.10	3.81	1.27	3.64	35.3°	37.75	9.327			26
	Plains, Va., "	0.8975	11.43	8.55	4.05	1.84	4.93	36.1°	36.86	9.362			27
	Armour & Co., best"	0.8984	12.98	10.82	4.04	1.30	3.94	33.5°	41.20	9.320			28
	" " " oleomargarine								49.91	9.601	No reaction		29
	" " " cheap "								51.34	9.646	" "		30
	½ Elgin and ½ Woodlawn No. 2								43.90	9.391			31
	" " " " "								48.01	9.416			32
	" " " " "								55.40	9.491			33
	Greensboro, N. C., sample[1]		7.81	8.52				37.5°	24.81				34

[1] Called butter.

exceedingly useful. The samples were forwarded to Prof. Atwater, prepared for combustion, without any description of their character being given except that they were fats. It is well understood that the estimation of the calories is of considerable use in a determination of the molecular weights of complex molecules and the results which we will report will serve to show, we, think, practical application of the use of the bomb calorimeter.

This is best seen by a study of the following tables, which give in detail the examinations that are ordinarily made for eleomargarine and butter (Table I.), and accompanying these examinations the calories per gram. The samples were prepared for these latter determinations by washing, melting, filtering, and drying the samples at 100° C.

The figures given by different authorities for butter fat, vary slightly. Stohman gives the heat equivalent as determined by the potassium chlorate method as 9.192 small calories per gram, while by the oxygen method it was 9.231 calories per gram. The three samples of pure butter burned were from the following sources: No. 28, the best butter used by Armour & Co., in the manufacture of butterine; No. 26, was Elgin Creamery butter; and No. 27, obtained from a Virginia gentleman, who sent it as a sample of the best butter made on his place. Nos. 31, 32, and 33, were mixtures of Elgin butter and oleomargarine. The figures obtained for butter fat are a little higher than those Stohman gives for pure butter.

Table II. The steady increase in the calories of the mixtures is in proportion to the amount of oleomargarine added to the butter and this taken in conjunction with the iodine number gives additional confirmatory evidence of the character of the sample.

TABLE II.

MIXTURE COMPOSED OF DEFINITE PROPORTIONS OF ELGIN AND WOODLAWN NO. 2.[3]

Sample.	Actual iodine equivalent.	Theoretical iodine equivalent.	Actual combustion calories per gram.	Theoretical combustion calories per gram.
¾ E and ¼ W, No. 2[3]...	43.90	43.76	9.391	9.412
½ F and ½ W, No. 2[3]...	48.01	48.77	9.416	9.498
¼ E and ¾ W, No. 2[3]...	55.40	55.78	9.491	9.584

The theoretical calories per gram for the above mixtures as compared with those found are,

	Theory.	Found.
No. 31	9.412	9.391
No. 32	9.498	9.416
No. 33	9.584	9.491

The actual combustion of the sample containing a small admixture of oleomargarine falls a little lower than theory requires, but is sufficiently high to indicate at once that there is adulteration of the normal butter. The other two samples give results still more distinctive and characteristic. The determination of the calories would be sufficient, therefore, to detect oleomargarine. If not relied upon entirely it still furnishes very satisfactory evidence. One point to which attention should be called is the exceedingly low temperature at which the oleomargarines melted. They were purchased at the end of winter and probably made to suit the winter trade. If left in an open dish in the laboratory for a few hours they became soft and semifluid.

In the case of the lards from various sources the results are somewhat different and are not so distinctive as compared with compound lard, as the butter and oleomargarine. (Table III.) Still even here the determination of the calories taken in conjunction with other determinations, as the iodine absorption, will also be of use. Should the determination of the calories show a low figure one could conclude that the lard was either a compound or a lard from the caul, intestines, or head of the animals, while the determination of the iodine number and cottonseed-oil test, would show at once whether the sample was a lard or a compound lard. The error of experiment in calorimetric work is usually counted at twenty-five calories per gram, but by careful work can be made less and a number of experiments in the same line as the above, would probably give data that would make the determination of the calories of still more practical value.

TABLE III.

ANALYSES OF SPECIMENS FROM ARMOR & CO.

Quality.	Melting point.	Iodine equivalent.	Combustion calories per gram.	Cotton-seed oil, Bechi's test.
Lard, leaf	....	56.85	9.621	none
" caul fat	40.0°	58.61	9.573	Slightly darken
" intestinal fat	40.7°	54.74	9.581	" "
" heads	29.5°	68.79	9.503	None.
" mixture of all fats ...	....	63.86	9.654	"
" trimmings ·	....	65.57	9.606	"
" compound, 1st grade	....	86.18	9.583	Purple brown.
" compound, 2nd grade	....	86.57	9.530	" "
" shield	....	61.01	9.598	None.
" special pure	37.5°	63.63	9.617	"

In a recent number of this Journal, September, 1895, Wess
has very carefully reviewed the subject of the determination
the iodine absorption number in pure and compound larc
claiming that the figures heretofore given for pure lard were t
low for the present methods of manufacture. This point al
came up for incidental consideration in connection with o
other examinations. We secured two sets of samples from Cł
cago, one sent direct from Armour & Co. (Table III), with tl
statement that the samples were what the names indicated. Tl
other set of samples was accompanied by a certificate from tl
inspector testifying to the character of the material as forwarde

TABLE IV.

ANALYSES OF LARDS FROM ARMOUR & CO.

Quality.	Iodine. equivalent.	Cotton-seed oil, Bechi's test.
Leaf	55.60	No reaction.
Caul fat	58.08	" "
Intestional fat	52.94	" "
Heads	62.36	" "
Trimmings	61.58	" "
Special pure	60.87	" "
Foreign shield	58.62	" "
Exp. Ref. Comp.	69.79	Purple black.
Prime steam	65.97	No reaction.
Dom. comp.	74.53	Purple black.

TABLE V.

Sample.	Iodine. equivalent.	Cotton-seed-oil, Bechi's test.	Combustion calories per gram.
Lard No. 5	58.98	....	....
Lard Plains	50.49	....	9.606
Cottolene	90.89	Purple black.	....

In addition two other samples of lard, one from Virginia, the other from Rhode Island, were examined. The samples sent with the inspectors' certificate were freshly made, while the other set was older material. There is a decided variation in the iodine equivalent and in deciding upon the character of the lard, the origin of the sample should undoubtedly be taken into consideration. As this is often not possible a check upon the other results may be secured by the determination of the calories.

BIOCHEMIC LABORATORY, WASHINGTON, D. C.,
December 14th, 1895

Discussion.—Mr. A. H. Sabin: I am very decidedly of the opinion that in investigations as to fats and oils, conclusive and satisfactory results can only be obtained by a comparison of methods. Such a method as this seems to me to be of a good deal of practical value because it is definite and positive. We make a combustion in this way and get some results which can be depended upon, and which can be verified; and the conditions are not difficult to duplicate. While I doubt if such a method will be of permanent value, because in such matters the ingenuity of the manufacturer is always pitted against the skill of the analyst, such a method always has weight, and must be taken in conjunction with other methods which also have weight and which also by themselves are not conclusive, but which have cumulative effect. I am certain that in regard to the vegetable fats it is only possible to arrive at just conclusions by a comparison of methods.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE. NO. 16.]

NOTE ON THE USE OF ACETYLENE GAS AS AN ILLUMINANT FOR POLARISCOPIC WORK.[1]

BY H. W. WILEY.

Received November 23, 1895

THROUGH the courtesy of Prof. Charles E. Munroe, I was able to secure twenty-five kilos of calcium carbide for

[1] Presented to the Washington Section, Dec. 9, 1895.

experimental purposes, together with four burners. The acetylene was developed by the action of water on the calcium carbide and conducted into a small gas meter from which it was burned under a pressure of water, the flame being regulated by a stop-cock. The quantity of gas furnished by the calcium carbide is illustrated by the following experiment:

From ninety-five grams of carbide 11.5 liters of gas were obtained measured at a temperature of 18°. It is thus seen that one kilo of the calcium carbide used would furnish a little over 226 liters of gas.

The rate at which the gas was burned for furnishing the illumination for the polariscope was measured and found to be one liter each four minutes, measured under a pressure of thirty inches of water. The actual pressure at which the gas was burned was very much less than this, being regulated by the stop-cock. The lamp was thus supplied at a rate of consumption amounting to fifteen liters per hour.

The illumination produced by the burning acetylene was used with a triple shadow Schmidt & Haensch double compensating polariscope and the accuracy of the readings with the intensely white light produced was tested with standard quartz plates. Two of the quartz plates read were standardized by the U. S. Coast and Geodetic Survey, in connection with this Division, and four were standardized by the Imperial German Commission of the Physical Institute at Berlin. The readings, to the nearest whole tenths, were as follows, at a temperature of 20°, which is slightly higher than that at which the quartz plates were standardized:

Coast Survey tube	92.06	read	92.1
" " "	99.06	"	99.1
German tube	74.45	"	75.4
" "	93.59	"	93.6
" "	100.36	"	100.3
" "	—91.70	"	—91.7

From the above readings it is seen that the light is absolutely reliable as tested against the best standards.

The degree of illumination was very great. The field of vision of the polariscope showed an intense illumination even at the neutral piont and yet permitted of the reading of the shadow at

the neutral point with the greatest accuracy. Three different observers in reading the quartz plates did not differ among themselves more than one-tenth of a degree.

A test was also made to determine the relative possibility of reading highly colored solutions with the acetylene light as compared with the ordinary kerosenes or gas illumination for the polariscope. A solution of " black strap" molasses was made, quite concentrated, without any clarifying agent whatever other than lead subacetate. The solution read in a 200 and 400 mm. tube gave a perfectly distinct shadow with the acetylene light permitting the reading to within one-tenth of a degree. With the kerosene or lamp light, the field of vision was almost obscured at the neutral point and the readings made by three different observers differed as much as three-tenths of a degree. Another solution was made with the same black strap molasses without the use of any clarifying agent other than alumina cream. This was diluted to such a degree as to be distinctly read to within one or two-tenths of a degree by the acetylene light. When an attempt was made to read this same solution by the ordinary source of illumination, it was found that the field of vision was absolutely obscured, no light whatever passing through.

The results of these observations show that the acetylene light is perfectly reliable for polarizing purposes, that it produces an intense degree of illumination permitting of a very delicate distinction between the shadow and the illuminated portions of the field of vision, and permits the reading of solutions so highly colored as to be perfectly obaque to the ordinary sources of light.

The above results suggest also the practicability of using the acetylene light for microphotographic purposes and for ordinary photography, but I have not made any tests of its actinic power. The light can also be used for projections. It is to be observed that with the small quantity of calcium carbide obtained, *viz.*, twenty-five kilos, there would be a sufficiency for almost a continuous polarization through a long period of time. With the cost of the calcium carbide known the actual cost of the light could be easily computed. I am ignorant, however, of the cos-

of the calcium carbide, it having been obtained for our use by the payment of the express charges only.

My thanks are due to Messrs. McElroy, Ewell, and Runyan for assistance in the preparation of the gas and in reading the polariscope.

INDIRECT ANALYSIS.

By Edward K. Landis.

Received December 23, 1895.

IN investigating this subject the author was struck with the difference in the formulas given in the text-books and on trying some of the cases found the results did not agree. Supposing that the old atomic weights used in the formulas were the cause of the trouble, it was thought best to derive a formula in such a manner that it would apply equally if the present weights should be modified, and it is given herewith, trusting that it may be useful to many chemists in cases where a separation of the two elements is difficult or tedious.

It will apply to any case where the atomic weights of the two elements are not the same, and the greater the difference between the atomic weights the greater the accuracy. Unfortunately, nickel and cobalt cannot be determined in this manner, but many other elements can be. This method is especially convenient for sodium and potassium, and probably more accurate than the separation with platinum chloride.

FIRST METHOD.

Data given :

Weight of mixture.

Weight of common constituent.

Let x = weight of salt with greatest per cent. of common constituent.

Let y = weight of salt with least per cent. of common constituent.

Let a = amount of common constituent in one part of x.

b = " " " " " " " " y.

W = weight of mixture.

w = " " common constituent.

To find x and y:

$$x+y = W, \qquad x = W-y,$$
$$ax + by = w,$$
$$a(W-y) + by = w,$$
$$a\,W-ay + by = w,$$
$$by-ay = w-a\,W,$$
$$(b-a)y = w-a\,W,$$
$$y = \frac{w-a\,W}{b-a},$$
$$x = \frac{w-b\,W}{a-b}.$$

$a-b =$ difference of coefficients of x and y.

Therefore, to find x or y, multiply the weight of mixture by the coefficient of the other salt. Find the difference between this and the weight of common constituent, and divide this result by the difference of the coefficients.

SECOND METHOD.

Same data as before and same symbols, except that here

$a =$ molecular weight of x.
$b =$ " " " y.

If all the common constituent were combined with y we should have a greater weight than W, and if combined with x less than W. In either case call this W'.

$$\text{Then} \frac{b}{a}\,x + \frac{b}{b}\,y = W',$$
$$\frac{a}{a}\,x + \frac{b}{b}\,y = W,$$

$$\text{Subtracting} \frac{b-a}{a}\,x = W'-W,$$
$$x = \frac{a(W'-W)}{b-a},$$
$$b-a : W'-W = a : x.$$

Rule.—Calculate the weight if common constituent were all combined with one of the salts. Find the difference between this and the weight of the two salts. Then the difference of the molecular weighls is to the difference found as the molecular

weight of the salt causing the difference is to the amount of that salt.

As an illustration let us take two grams sodium chloride and one gram potassium chloride with the following data:

$$\begin{aligned} Cl &= 35.45 \\ Na &= 23.05 \\ K &= 39.11 \\ KCl &= 47.5456 \text{ per cent. chlorine.} \\ NaCl &= 60.598 \quad \text{''} \qquad \text{''} \end{aligned}$$

FIRST METHOD.

$W=3$,

$w=1.687416$, $\qquad x=NaCl$,

$a=0.60598$, $\qquad y=KCl$,

$b=0.475456$,

$$x=\frac{w-bW}{a-b}=\frac{1.687416-1.426368}{0.130524}=2,$$

$$y=\frac{w-aW}{a-b}=\frac{1.81794-1.687416}{0.130524}=1.$$

Crookes gives the following formula:

Let W = weight of mixed chlorides.

C = " " chlorine.

$NaCl = C \times 7.6311 - W \times 3.6288.$

$KCl = W \times 4.6288 - C \times 7.6311.$

Using the data above this gives $NaCl = 1.9904$, $KCl = 1.0096$.

The above formula should read

$NaCl = 7.6311\ C - 3.6288\ W$ to be perfectly clear, otherwise it means that C is multiplied by 7.6311, W subtracted from the product and the result multiplied by 3.6288, which would not give the answer.

Bailey's Chemist's Pocket Book (3rd edition) gives the following:

$$NaCl = \left((C \times 2.0129) - W\right) \times 3.6288.$$

Using the same data this gives $NaCl = 1.990277$ instead of 2.0.

SECOND METHOD.

Calculating Cl to KCl.

$$Cl = 1.687416,$$
$$W = 3,$$
$$\frac{1.687416}{0.475456} = 3.540047\ KCl$$
$$3.549047 - 3.0 = 0.549047,$$
$$\frac{0.549047 \times 58.5}{74.56 - 58.5} = NaCl = 2.$$

Calculating Cl to NaCl.

$$\frac{1.687416}{0.60598} = 2.7846\ NaCl,$$
$$3.0 - 2.7846 = 0.2154,$$
$$\frac{0.2154 \times 74.56}{74.56 - 58.5} = KCl = 1.$$

The author hopes that this may prove the accuracy of the method and that it may be extensively used.

The preceding applies to mixtures of two substances only; now let us consider the case of three. If we have iodine, bromine and chlorine in the same liquid, how are we to arrive at the amounts of each? We may consider two cases, one given in Woodward's Chemical Arithmetic and the other in Crookes' Select Methods, the second being exactly the opposite of the first. Three equal portions of a liquid containing chlorine, bromine and iodine are taken. No. 1 is precipitated with silver nitrate and precipitated of silver iodide, silver bromide and silver chloride weighed. No. 2 is precipitated in the same manner, but digested with potassium bromide until all chlorine is replaced by bromine, then weighed. No. 3 is likewise precipitated and digested with potassium iodide until entirely converted into silver iodide, then weighed. In Crookes' example the iodine is replaced by bromine and the bromine by chlorine. In the first case the weights increase. and in the second they decrease.

Now suppose we try to derive a formula for each of these cases, beginning with Woodward's and using the same data as before, also Ag = 108, I = 127, Br = 80.

Woodward's Chemical Arithmetic.

Mixture of silver iodide, silver chloride and silver bromide.

$$AgI + AgBr + AgCl = W,$$
$$AgI + AgBr + AgBr = W',$$
$$AgI + AgI + AgI = W''.$$

Let $x = AgCl$, $a =$ molecular weight.
$y = AgBr$, $b =$ " "
$z = AgI$, $c =$ " "

$$x + y + z = W,$$
$$\frac{b}{a}x + y + z = W',$$
$$\frac{c}{a}x + \frac{c}{b}y + z = W'',$$
$$x = \frac{a(W' - W)}{b - a},$$
$$y = \frac{b(W'' - W')}{c - b} - \frac{b(W' - W)}{b - a},$$
$$z = W' - \frac{b(W'' - W')}{c - b}.$$

Crookes', same data:

$$AgI + AgBr + AgCl = W,$$
$$AgBr + AgBr + AgCl = W',$$
$$AgCl + AgCl + AgCl = W'',$$
$$x + y + z = W,$$
$$x + y + \frac{b}{c}z = W',$$
$$x + \frac{a}{b}y + \frac{a}{c}z = W'',$$
$$z = \frac{c(W - W')}{c - b},$$
$$y = \frac{b(W' - W'')}{b - a} - \frac{b(W - W')}{c - b},$$
$$x = W' - \frac{b(W' - W'')}{b - a}.$$

FIRST METHOD.

Woodward's Example:

$W = 27.19$, $W' = 30.87$, $W'' = 36.73$, $a = 143.45$, $b =$
$c = 235$.

$$x = \frac{143.45 \times 3.68}{44.55} = 11.8495 \text{ AgCl} = 2.9282 \text{ Cl}$$

$$y = \frac{188 \times 5.96}{47} - \frac{188 \times 3.68}{44.55} = 8.3105 \text{ AgBr} = 3.5363 \text{ Br},$$

$$z = 30.87 - \frac{5.96 \times 188}{47} = 7.03 \text{ AgI} = 3.799 \text{ I}.$$

Crookes' Example:

$W = 15.57$, $W' = 14.69$, and $W'' = 12.20$,

$$z = \frac{235 \times 0.88}{47} = 4.4 \text{ AgI},$$

$$y = \frac{188 \times 2.49}{44.55} - \frac{188 \times 0.88}{47} = 6.9877 \text{ AgBr},$$

$$x = 14.69 - \frac{188 \times 2.49}{44.55} = 4.1823 \text{ AgCl}.$$

SECOND METHOD.

Woodward's Example:

$$\text{AgCl} + \text{AgBr} + \text{AgI} = 27.19,$$
$$\text{AgBr} + \text{AgBr} + \text{AgI} = 30.87,$$
$$\text{AgI} + \text{AgI} + \text{AgI} = 36.83,$$
$$30.87 - 27.19 = 3.68,$$
$$44.55 : 3.68 = 143.45 : x = 11.8495 \text{ AgCl}.$$

Now $11.8495 \text{ AgCl} = 15.5295 \text{ AgBr} = 19.41187 \text{ AgI}$,

$$27.19 - 11.8495 = 15.3405,$$
$$36.83 - 19.41187 = 19.41813.$$

Therefore $\text{AgBr} + \text{AgI} = 15.3405$,

$$\text{AgI} + \text{AgI} = 17.41813,$$
$$17.41813 - 15.3405 = 2.07763,$$
$$47 : 2.07763 = 188 : x = 8.3105 \text{ AgBr}.$$

Adding the AgCl and AgBr thus found and subtracting their sum from 27.19, we get AgI = 7.03.

Comparison of results:

	Woodward.	First method.	Second method.
Cl	2.92	2.9283	2.9283
Br	3.51	3.5363	3.5363
I	3.69	3.799	3.799

Crookes' Example:

$$AgCl + AgBr + AgI = 15.57,$$
$$AgCl + AgBr + AgBr = 14.69,$$
$$AgCl + AgCl + AgCl = 12.20,$$
$$15.57 - 14.59 = 0.88,$$
$$47 : 0.88 = 235 : x = 4.4 \text{ AgI}.$$

Now $4.4 \text{ AgI} = 3.52 \text{ AgBr} = 2.68586 \text{ AgCl}$,

$$15.57 - 4.4 = 11.17,$$
$$12.20 - 2.68586 = 9.51414.$$

Therefore $AgCl + AgBr = 11.17$,

$$AgCl + AgCl = 9.51414,$$
$$11.17 - 9.51414 = 165586,$$
$$44.55 : 1.65586 = 188 : x = 6.9877 \text{ AgBr}.$$

Adding the AgI and AgBr thus found and subtracting their sum from 15.57, we get 4.1823 AgCl.

Comparison of results:

	Crookes.	First method.	Second method.
AgI	4.4	4.4	4.4
AgBr	6.998	6.9877	6.9877
AgCl	4.172	4.1823	4.1823

It will readily be seen that the first method requires less work than the second, and has the advantage of giving any of the three without the necessity of finding the others.

No orginality is claimed for the foregoing, but the matter has been put in such a shape that it may be applied to any case, and any atomic weights may be used, thus making its application universal. In special cases it may be condensed by finding the factors by which to multiply the weights directly instead of multiplying by one number and dividing by another, but it was thought best to give the entire work as a help to those not conversant with algebra.

The writer would like to impress upon chemists the importance of giving the atomic weights and factors used in all calculations, so that their figures may be checked and errors avoided. As the atomic weights vary, important work may be recalculated and thus retain its value.

NOTE ON THE MICROSCOPIC DETECTION OF BEEF FAT IN LARD.[1]

By Thomas S. Gladding.

Received January 3, 1896.

IN the preparation of crystals of lard and beef stearin for microscopic examination, I find the following method gives excellent results, the crystals being of good size and of distinctive form. Dissolve five cc. of melted lard in a mixture of ten cc. alsolute alcohol and five cc. ether, in a small Erlenmeyer flask, heating gently if necessary. Place a plug of cotton in the mouth of the flask and allow to stand in a cool place for about half an hour. The stearin crystallizes out, the olein remaining in solution. Filter rapidly through a paper wet with alcohol, using a filter pump, and wash crystals and paper once with the above alcohol-ether mixture (10-5). Let the crystals dry in the air and remove them from the paper to the flask. Dissolve in twenty-five cc. of ether, replace the cotton plug, and place the flask in a slanting position in a large beaker (about one liter) nearly full of water. Keep this in a cool place over night. The ether evaporates very slowly and the crystals of stearin are gradually formed in the solution, the large quantity of water surrounding the ether solution guarding against any sudden change of temperature. For valuable plates giving characteristic forms of lard stearin crystals and beef stearin crystals reference is made to Bulletin No. 13, Part IV., Division of Chemistry, U. S. Department of Agriculture.

NOTES.

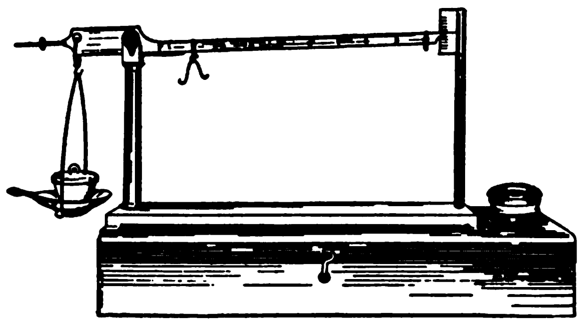
The Estimation of Levulose in Honey.—Through my negligence, I failed to call attention, on page 81 of the January number, to the optical method described by Allen, Commercial Organic Analysis, Vol. 1, p. 291, relating to the estimation of levulose by changes in the specific rotatory power due to variations of temperature.

H. W. Wiley.

A New Balance for First Year's Work in General Chemistry.—The little balance shown in the cut was designed for the use

[1] Read at the Cleveland meeting, December 31, 1895.

of my students in their first year's laboratory prac
and has served its purpose so well in two large classes t
venture to call attention to it in the hope that others may fi



it a satisfactory solution of the balance problem in their sch
of beginners' laboratory work.

It is simple, efficient, and not expensive. The posts
beam are of lacquered brass ; the base of iron. The leng
the beam is twelve inches. The riders are of there wei
equivalent, when at the first division of the long arm, to 1
0.100 and 0.010 gram respectively in the pan. Thus, in the
the weight of the crucible is 12.230 grams. The balance is
tive to 0.010 with a load of 30.000 grams, and to 0.005 gram
a smaller load. Adjustment to zero before weighing is eff
by means of a nut at the end of the short arm. It ma
obtained of Messrs. Richards & Co., of New York.

JOHN TAPPAN STODDA

NEW BOOKS.

ANALYTICAL CHEMISTRY. BY N. MENSCHUTKIN, PROFESSOR IN
UNIVERSITY OF ST. PETERSBURG. Translated from the Third G
Edition, under the Supervision of the Author, by James Locke.
don and New York : Macmillan & Co. 512 pp. Price $4.00.

Although the plan of treating the whole subject of anal
chemistry, qualitative and quantitative, in one volume has
ous merits, it is nevertheless something of a novelty, in
country at least, and on this and many other accounts this t
lation of Professor Menschutkin's work is very welcome.

It is not a book that can be used to the best advantage without good accompanying and supplementary instruction, and this is not because it is incomplete or unduly concise, but because the ideals and aims of the author are high ones, and the teacher is constantly needed to read between the lines. Principles are dealt with from the very first to the last and the *rationale* of the method is the point on which stress is laid. In the first part of the preface the author sets forth briefly his views as to the value of analytical work in a course of chemical study. His recommendation that it be not taken up too early is especially to be commended, as is also the plan of laying great stress upon the development of methods by the student himself, a practice altogether too uncommon.

The first 280 odd pages of the book deal with qualitative analysis. In its treatment of this difficult subject it differs markedly from the majority of treatises. There are no "tables" or "schemes." Each group of metals is first carefully studied with reference to its distinguishing group characteristics. Afterward the special properties and reactions of the individual members are taken up, and finally the analytical process deduced from the results. The plan of frequently giving solubilities quantitatively is a very helpful one. There are a few curious mistakes; for example, it is stated on p. 32 that potash alum is *less soluble* than the cesium and rubidium alums. The chromium bead is spoken of as *blue* instead of green (p. 70). This is evidently a slip of the pen, as the color is correctly given a few lines further on. Again on p. 126, in describing the analysis of columbite and tantalite, the mixture of oxides obtained by fusing the mineral with acid potassium sulphate and boiling out with water is said to be treated with ammonium sulph*ite*, instead of sulph*ide*. This, however, appears to be a misprint, as shown by the context. The word oxide is frequently used where hydroxide is meant.

The remaining 230 pages are devoted to quantitative analysis. This part of the book is treated in three sections. I. Gravimetric Analysis. II. Volumetric Analysis. III. Organic Analysis. In the first section the metals and metalloids are dealt with according to the following general plan: First the methods

are given for determining each individual of the group, t the methods for separating the different members of the gr from each other. This is a better plan than the more comı one of giving all the determinations first and afterwards all separations.

The descriptions and directions are decidedly concise, sufficient for the needs of fairly advanced students. Begin will need and should in any case have considerable supplen tary instruction. The non metals are treated according to same general plan. A chapter of "operations and exampl follows, which might perhaps have been put with more profi the beginning instead of the end of the section.

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ON THE DENSITIES OF OXYGEN AND HYDROGEN AND ON THE RATI THEIR ATOMIC WEIGHTS. BY EDWARD W. MORLEY. 1895: Smith ian Contributions to Knowledge. 4°. Forty cuts. xii., 117 Price, $1.00.

The ratio between oxygen and hydrogen is, to speak figı tively, the base-line upon which our entire system of ato weights depends. But few of the other elements can be rea compared with hydrogen directly; practically all of them referred to hydrogen through the intervention of oxygen; so the atomic weight of the latter needs to be known with utmost accuracy. A small error here becomes cumulative w introduced into the computation of higher values, and in case of uranium it is multiplied to fifteen times its original m nitude.

Ten years ago the atomic weight of oxygen seemed tc pretty well known, and stood very nearly at 15.96. This, h

ever, was near enough to the round number 16 to suggest that the difference might be due to error, and therefore reinvestigation began. First came Cooke and Richards, then Keiser, Noyes, Rayleigh, Dittmar and Henderson, and Leduc. Of these, Keiser alone approximated to the old value, finding O = 15.95. All of the others obtained results ranging from 15.866 to 15.897, with an outstanding uncertainty still larger than could long be tolerated. This uncertainty, thanks to Professor Morley, is now thrown into the third or fourth decimal place, and need no longer be troublesome.

The first and second divisions of Morley's monograph relate to the densities of the two gases, and are most elaborate in their details. Every precaution was taken to insure the purity of the material used, the methods of manipulation were varied, and every conceivable source of error seems to have been foreseen and guarded against.

For oxygen, three series of determinations are given. In the first series, the pressure and temperature of the gas to be weighed were determined by mercurial thermometers and a manobarometer. In the second series, pressure and temperature were not observed for each experiment, but were made equal to the temperature and pressure of a standard volume of hydrogen, comparison being made by means of a differential manometer. In the third series the temperature was that of melting ice, and pressure alone was observed. For the weight of one liter of oxygen, at 0°, 760 mm., at sea level and in latitude 45°, the three series give as follows, in grams :

Series 1,	9 experiments,	1.42879 ± 0.000034
" 2,	15 "	1.42887 ± 0.000048
" 3,	17 "	1.42917 ± 0.000048

On experimental grounds, Morley regards the third series as the best, and assigns it double weight. On this basis the general mean becomes

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For hydrogen, five series of determinations were made. In the first, the manipulations were like those of the first oxygen

series, with which it was strictly parallel. In the second, the weighing globes were surrounded by melting ice, and pressure was measured with a siphon barometer. In the third series the hydrogen was weighed, not in the globes where its pressure, temperature, and volume were taken, but before its introduction into them. Globes having a joint capacity of forty-two liters were connected together, for this series, and the hydrogen was weighed in palladium, of which 600 grams were used. The fourth and fifth series resembled the third. The hydrogen used was electrolytic. The results are subjoined, for the weight of one liter of hydrogen, in grams:

Series 1,	15	experiments,	0.089938 ± 0.000007
" 2,	19	"	0.089970 ± 0.000011
" 3,	8	"	0.089886 ± 0.0000049
" 4,	6	"	0.089880 ± 0.0000088
" 5,	11	"	0.089866 ± 0.0000034

In series 1 and 2, which Morley rejects, the hydrogen may have been contaminated by traces of mercurial vapor. In the remaining series that impurity was not present in the weighing of the gas, and exerts no influence upon the final result. Furthermore, in these series, stop-cocks were not used, and the connections were made by fusing the glass tubes into an unbroken continuity. The mean of series 4, 5, and 6 is

$$0.089873 \pm 0.0000027,$$

and this is undoubtedly the best value yet found for the weight of a liter of hydrogen. Dividing this into the weight of oxygen, we have as the ratio of densities,

$$O = 15.9002.$$

In order to derive from this value the atomic weight of oxygen, the volumetric composition of water must be known. This subject forms the third part of Morley's memoir. He decomposed water by electrolysis, determined the density of the electrolytic mixed gases, and from that calculated the datum sought. The result is that in water, hydrogen and oxygen are combined in the ratio by volume of

$$2.00269 : 1.$$

Applying this ratio to the correction of the density ratio, we have

$$O = 15.879,$$

for the atomic weight of oxygen as given by the density method.

In the fourth part of the memoir Morley describes his gravimetric syntheses of water, which are the first really complete syntheses yet recorded. That is, nothing is taken by difference; hydrogen was weighed, oxygen was weighed, and the water formed was weighed, and all directly. By weighing the hydrogen in palladium, over three and eight-tenths grams could be taken in one experiment, a quantity which would be unmanageable in any attempt to weigh it in globes. Globes, however, were used for weighing the heavier oxygen; and the two gases were caused to combine by sparking in a suitable combustion apparatus. After combustion was complete, the apparatus containing the water was weighed, and the residual excess of gases left unburned was analyzed. The use of stop-cocks, in transferring the gases to the combustion apparatus, was completely avoided. Errors due to leakages, therefore, did not occur.

In all, twelve syntheses were made. Each one gives two values for the atomic weight of oxygen, except in one case, when the apparatus was broken. One value is derived from the weights of hydrogen and oxygen, the other from the weights of hydrogen and water. They are as follows:

	H : O.	H : H_2O.
	15.878	15.877
	15.881	15.878
	15.878	15.873
	15.880	lost
	15.877	15.881
	15.877	15.876
	15.877	15.875
	15.878	15.879
	15.879	15.881
	15.881	15.883
	15.881	15.883
	15.882	15.878
Mean,	15.8792	15.8785

The average of there two means is 15.87885, a result practically identical with that derived from the gaseous densities. The value, 15.879, then, is to be taken as the nearest approximation to the true atomic weight of oxygen, and this, for ordinary purposes, may be rounded off to 15.88.

It is hard to express an opinion concerning this great investigation, without seeming to be extravagant. In thoroughness, foresight, and manipulative skill it stands in the very front rank of chemical investigations, and on the same plane with the classical researches of Stas. In short, it is doubtful whether any better work of its kind has ever been published, and it has very few peers. To fully appreciate the memoir it must be studied in detail and at first hand ; even Morley's own abstracts in various chemical journals fail to give an adequate impression of the magnitude of his achievement. The paper may at once take its place among "the classics of the exact sciences."

F. W. CLARKE.

BOOKS RECEIVED.

Bulletin No. 41. Agr. Expt. Sta. Univ. of Minn. SOILS. Minneapolis. Minn. 1895, 79 pp. (1). The Essential Elements of Soil Fertility. (2). Humus as a Factor of Soil Fertility. (3). The Chemical and Mechanical Analysis of Soils. (4). The Action of Organic and Mineral Acids upon Soils. (5). Comparison of Different Methods of Farming upon the Conservation of Soil Fertility.

The Educational Value of Engineering Studies. An address delivered on Founder's Day, Oct. 10, 1892, by Thomas M. Drown, LL.D. Lehigh University, Bethlehem, Pa. 1895. 30 pp.

The Chemist's Compendium. Complied by C. J. S. Thompson. New York: Macmillan & Co. 1896. viii, 230 pp. Price $1.00.

Practical Inorganic Chemistry. By G. S. Turpin, M. A., D. Sc., London and New York ; Macmillan & Co., 1895. viii, 156 pp. Price 60 cents.

Bulletin No. 39. Analysis of Commercial Fertilizers. Baton Rouge: Agr. Expt. Sta. of La. 22 pp.

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VOL. XVIII. [MARCH, 1896.] No. 3.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THIRD ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1895.[1]

BY F. W. CLARKE.

Received January 3, 1896.

To the Members of the American Chemical Society:

YOUR committee upon atomic weighis respectfully submits the following report, summarizing the work done in this branch of chemistry during 1895, a year which may be well called eventful in the history of the science. Two new elements, argon and helium, have been made known to the world, and from the most unexpected sources; the collective works of Stas have been published by the Belgian Academy, as a monument to his memory; Prof. Morley's great research upon oxygen is at last finished; and a goodly number of other important determinations have appeared. Incidentally, but pertinently, I may also call attention to the Marignac memorial lecture by Cleve,[2] in which the atomic weight researches of the former chemist are well outlined; and to the extraordinary number of papers upon the periodic law, which have been called out by the discovery of argon and helium. These papers fall outside the scope of this report, and they are numerous enough to almost warrant a bibliography of their own.

The H : O ratio.—Prof. Morley's work upon this fundamental constant has been published in full by the Smithsonian Insti-

[1] Read at the Cleveland Meeting, December 31, 1895.

[2] *J. Chem. Soc.*, June, 1895.

tute,[1] and divides itself naturally into four parts: First, the density of oxygen; second, that of hydrogen; third, the volumetric composition of water; and fourth, its gravimetric synthesis.

For the density of oxygen, or rather the weight of one liter at 0°, 760 mm., at sea level and in latitude 45°, three sets of measurements are given, with the following mean values in grams:

Series 1	1.42879 ± 0.000034
" 2	1.42887 ± 0.000048
" 3	1.42917 ± 0.000048

As the third series, on experimental grounds, is regarded by Morley as the best, he assigns it double weight, and on this basis the general mean of all three becomes

$$1.42900 \pm 0.000034.$$

For the weight of a liter of hydrogen, under similar standard conditions, five series of determinaiions are given, as follows:

Series 1	0.089938
" 2	0.089970
" 3	0.089886 ± 0.0000049
" 4	0.089880 ± 0.0000088
" 5	0.089866 ± 0.0000034

The hydrogen of the first and second series was probably contaminated by traces of mercurial vapor, and these results are therefore rejected by Morley. For the third, fourth and fifth series the electrolytic gas was occluded in palladium and transferred to the measuring globes without the intervention of stop-cocks; thus avoiding contact with mercury and leakages of external air. Their general mean is

$$0.089873 \pm 0.0000027.$$

Dividing the weight found for oxygen by this value for hydrogen the ratio becomes

$$15.9002.$$

For the volumetric ratio O : 2H, Morley finds the value

[1] "On the densities of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights." By Edward W. Morley. Smithsonian Contributions to Knowledge, 1895. 4to. xi + 117 pp. 40 cuts. Abstract in *Am. Chem. J.*, 17, 267, (gravimetric); and *Ztschr. phys. Chem.*, 17, 87, (gaseous densities); also note in *Am. Chem. J.*, 17, 396.

1 : 2.00269. Applying this as a correction to the density ratio, we have for the atomic weight of oxygen

$$O = 15.879.$$

In his synthesis of water Morley differs from all of his predecessors in that he weighed both constituents separately, and also the water formed. In other words, his syntheses are complete, and take nothing for granted. The weights in gram are as follows:

	O used.	H used.	Water found.
1	25.9176	3.2645	29.1788
2	25.8531	3.2559	29.1052
3	30.3210	3.8193	34.1389
4	30.5294	3.8450	Lost.
5	30.4700	3.8382	34.3151
6	30.5818	3.8523	34.4327
7	30.4013	3.8297	34.2284
8	30.3966	3.8286	34.2261
9	30.3497	3.8225	34.1742
10	30.3479	3.8220	34.1743
11	29.8865	3.7637	33.6540
12	30.3429	3.8211	34.1559

From these data, two sets of values for the atomic weight of oxygen are derivable; one from the ratio H : O, the other from the ratio H : H_2O. These sets are subjoined.

	H : O.	H : H_2O.
1	15.878	15.877
2	15.881	15.878
3	15.878	15.873
4	15.880	......
5	15.877	15.881
6	15.877	15.876
7	15.877	15.875
8	15.878	15.879
9	15.879	15.881
10	15.881	15.883
11	15.881	15.883
12	15.882	15.878
Mean	15.8792	15.8785

From the densitv work the value found was 15.879, and the mean of this with the two synthetic results is

$$O = 15.8789.$$

Hence, for all practical purposes, the atomic weight of oxygen may be put at 15.88, with an uncertainty of less than one unit in the second decimal.

It is impracticable, in a report of this kind, to go into the details of so elaborate an investigation as this of Morley's, and a bare statement of results must suffice. The research, however, is one of the most perfect of its kind, every source of error having been considered and guarded against, and it will doubtless take its place in chemical literature as a classic. Independently of its main purpose, the book is almost a manual on the art of weighing and measuring gases, and no experimenter who engages upon work of that kind can afford to overlook it.

More recently still, a new determination of the atomic weight of oxygen has been published by Julius Thomsen,[1] whose method is quite novel. First, aluminum, in weighed quantities, was dissolved in caustic potash solution. In one set of experiments the apparatus was so constructed that the hydrogen evolved was dried and then expelled. The loss of weight of the apparatus gave the weight of the hydrogen so liberated. In the second set of experiments the hydrogen passed into a combustion chamber in which it was burned with oxygen, the water being retained. The increase in weight of this apparatus gave the weight of oxygen so taken up. The two series, reduced to the standard of a unit weight of aluminum, gave the ratio between oxygen and hydrogen.

The results of the two series, reduced to a vacuum and stated as ratios, are as follows:

$$\text{First, } \frac{\text{Weight of H.}}{\text{Weight of Al.}} \qquad \text{Second, } \frac{\text{Weight of O.}}{\text{Weight of Al.}}$$

First.	Second.
0.11180	0.88788
0.11175	0.88799
0.11194	0.88774
0.11205	0.88779
0.11189	0.88785
0.11200	0.88789
0.11194	0.88798
0.11175	0.88787

[1] *Ztschr. anorg. Chem.*, 11, 14.

First.	Second.
0.11190	0.88773
0.11182	0.08798
0.11204	0.88785
0.11202	———
0.11204	0.88787 ± 0.000018
0.11179	
0.11178	
0.11202	
0.11188	
0.11186	
0.11185	
0.11190	
0.11187	
———	
0.11190 ± 0.000015.	

Dividing the mean of the second column by the mean of the first, we have for the equivalent of oxygen:

$$\frac{0.88787 \pm 0.000018}{0.11190 \pm 0.000015} = 7.9345 \pm 0.0011.$$

$$\text{Hence, } O = 15.8690 \pm 0.0022.$$

The details of the investigation are somewhat complicated, and involve various corrections which need not be considered here. The results as stated, includes all corrections and is evidently good. The ratios, however, cannot be reversed and used for measuring the atomic weight of aluminum, because the metal employed was not absolutely pure.

The Stas Memorial.—As a monument to the memory of the late Jean Servias Stas, more appropriate than statue or column of stone, the Belgian Academy has published his collected works in three superb quarto volumes.[1] All of his great investigations are here gathered together, and in the third volume, entitled "Oeuvres Posthumes," some hitherto unpublished data are given for the important ratio between potassium chloride and silver. These data are represented by two series: one made with a uniform sample of silver, and chloride from various sources; the other with constant chloride, but with silver of diverse origin; the aim being to establish experimentally the fixed character of each substance. The first series is complete;

[1] Jean Servias Stas. Oeuvres Complétes. Edited by W. Spring. Bruxelles, 1894.

of the second series only one experiment was found recorded among Stas' papers.

The quantity of potassium chloride equivalent to 100 parts of silver was found to be as follows:

	69.1227
	69.1236
	69.1234
	69.1244
	69.1235
	69.1228
	69.1222
	69.1211
	69.1219
	69.1249
	69.1238
	69.1225
	69.1211
Mean of first series	69.1229
Second series	69.1240

These results give an effective confirmation to Stas' determinations of 1882.

Cobalt.—The atomic weight of cobalt has been redetermined by Thiele.[1] First, carefully purified oxide of cobalt, CoO, was reduced in hydrogen. The weight and results are as follows:

Residual Co.	Loss of O.	Atomic weight of Co.
0.90068	0.24429	58.843
0.79159	0.21445	58.912
1.31558	0.35716	58.788
	Mean	58.848

Reduced to vacuum standards this becomes

$$Co = 58.826,$$

when $O = 15.96$.

In a second method metallic cobalt was dissolved in hydrochloric acid, and the solution evaporated to dryness with special precautions against dust. The chloride thus obtained was then dried at 150° in a stream of pure gaseous hydrochloric acid, so that basic salts could not be formed. From the weight of cobalt

[1] "Die Atomgewichts Bestimmung des Kobalts." A doctoral dissertation. Basel, 1895.

and of cobalt chloride the ratio $Co : Cl_2$ is determined. The chlorine was afterwards re-estimated as silver chloride, giving the ratio Co : 2AgCl. The weights are subjoined :

Co taken.	Cl taken up.	AgCl.
0.7010	0.8453	......
0.3138	0.3793	......
0.2949	0.3562	1.4349
0.4691	0.5657	2.2812
0.5818	0.7026	2.8303
0.5763	0.6947	......
0.5096	0.6142	2.4813

Hence, with Cl = 35.37, and Ag = 107.66, Co =

$Co : Cl_2$.	Co : 2AgCl.
58.66	......
58.52	......
58.57	58.828
58.66	58.825
58.58	58.803
58.68	......
58.69	58.750
Mean 58.64	Mean, 58.801

The second column is subject to a small correction for dissolved silver chloride, which reduces the mean to Co = 58.770. Reduced to a vacuum this becomes 58.765, and the value from the Co : Cl_2 ratio becomes 58.61. Thiele regards Co = 58.765 as the most probable value to be derived from his experiments. This becomes

$$\text{With } O = 16, \qquad Co = 58.912$$
$$\text{'' } O = 15.88, \qquad Co = 58.470.$$

In my report for 1894 I gave Winkler's work on cobalt and nickel, which involved their ratios to iodine. In a supplementary paper Winkler[1] gives some similar experiments with iron, intended to show that errors due to metallic occlusion of hydrogen are absent from his determinations. He succeeds in proving that such errors, if they exist, must be very small. Thiele also considered their possibility, and guarded against them in the preparation of his cobalt.

Zinc.—Atomic weights redetermined by Richards and Rogers,[2]

[1] *Ztschr. anorg. Chem.*, 8, 291.

[2] *Ztschr. anorg. Chem.*, 10, 1. Calculations made with O = 16, Ag = 107.93, and Br = 79.955.

who used the bromide method. Zinc bromide, carefully pi
fied, was treated gravimetrically with standard silver soluti
The weights and results are subjoined :

First, $ZnBr_2 : 2AgBr$.

$ZnBr_2$.	AgBr.	Atomic weight o
1.69616	2.82805	65.469
1.98198	3.30450	65.470
1.70920	2.84549	65.487
2.35079	3.91941	65.470
2.66078	4.43751	65.400
	Mean,	65.459

Second, same ratio.

$ZnBr_2$.	AgBr.	Atomic weight o
2.33882	3.90067	65.400
1.97142	3.28742	65.434
2.14985	3.58539	65.402
2.00966	3.35074	65.463
	Mean,	65.425

Third, $ZnBr_2 : Ag_2$.

$ZnBr_2$.	Ag.	Atomic weight o
2.33882	2.24063	65.409
1.97142	1.88837	65.444
2.14985	2.05971	65.396
2.00966	1.92476	65.472
	Mean,	65.430

Two additional series of data are given by Richards alone,
follows :

First, $ZnBr_2 : Ag_2$.

$ZnBr_2$	Ag.	Atomic weight of
6.23833	5.9766	65.403
5.26449	5.0436	65.404
9.36283	8.9702	65.392
	Mean,	65.402

Second, $ZnBr_2 : 2AgBr$.

$ZnBr_2$.	AgBr.	Atomic weight of
2.65847	4.43358	65.410
2.30939	3.85149	65.404
5.26449	8.77992	65.404
	Mean,	65.406

The final mean adopted by Richards is 65.404. With O = 15.88 this becomes

$$Zn = 64.913.$$

Cadmium.—Mr. Bucher's paper,[1] as its title indicates, is a study of methods rather than a final determination of atomic weight; but the results recorded in it compare well with those reached by others. His starting point is metallic cadmium, purified by nine distillations *in vacuo*, and from this material, with pure reagents, his various preparations were made. Vacuum weights are given, and the antecedent values used in calculation are O, 16; S, 32.059; C, 12.003; Cl, 35.45; Br, 79.95; and Ag, 107.93.

First, cadmium oxalate, dried for fifty hours at 150°, was decomposed by heat, and so reduced to oxide. The variations are mainly attributed to imperfect dehydration of the oxalate. Weights and results are as follows:

Oxalate.	Oxide.	Atomic weight of Cd.
1.97674	1.26474	111.74
1.94912	1.24682	111.83
1.97686	1.25886	111.85
1.87099	1.19675	111.81
1.37550	0.87994	111.86
1.33313	0.85308	111.96
1.94450	1.24452	112.02
2.01846	1.29210	112.09
	Mean,	111.89

Second, cadmium oxalate was transformed to sulphide by heating in a stream of hydrogen sulphide. The data are:

Oxalate.	Sulphide.	Atomic weight of Cd.
2.56319	1.84716	112.25
2.18364	1.57341	112.19
2.11643	1.52462	112.03
3.13105	2.25582	112.12
	Mean,	112.15

Third, cadmium chloride, dried at 300° in a stream of dry, gaseous hydrochloric acid, was precipitated by silver nitrate, and the silver chloride was collected with all necessary precautions. The weights and results are subjoined:

[1] "An examination of some methods employed in determining the atomic weight of cadmium." By John E. Bucher. Johns Hopkins University, doctoral dissertation. Baltimore (Friedenwald), 1895.

$CdCl_2$.	AgCl.	Atomic weight of Cd.
3.09183	4.83856	112.34
2.26100	3.53854	112.33
1.35729	2.12431	112.32
2.05582	3.21727	112.34
1.89774	2.97041	112.31
3.50367	5.48473	112.28
2.70292	4.23087	112.30
4.24276	6.63598	112.44
3.40200	5.32314	112.37
4.60659	7.20386	112.47
2.40832	3.76715	112.42
2.19144	3.42724	112.46
2.84628	4.45477	112.32
2.56748	4.01651	112.41
2.31003	3.61370	112.41
1.25008	1.95652	112.32
1.96015	3.06541	112.47
2.29787	3.59591	112.45
1.94227	3.03811	112.42
1.10976	1.73547	112.47
1.63080	2.55016	112.48
	Mean,	112.39

Fourth cadmium bromide was analyzed in much the same way as the chloride. The weights and results are as follows:

$CdBr_2$.	AgBr.	Atomic weight of Cd.
4.39941	6.07204	112.35
3.18030	4.38831	112.42
3.60336	4.97150	112.45
4.04240	5.58062	112.29
3.60505	4.97319	112.38
	Mean,	112.38

Fifth, cadmium sulphate was formed by synthesis from metallic cadmium. 1.15781 grams cadmium gave 2.14776 cadmium sulphate. Hence Cd = 112.35. As any impurity in the sulphate would tend to lower the atomic weight found, this is probably a minimum valve.

Sixth, metallic cadmium was converted into oxide by solution in nitric acid and ignition of the nitrate. The ignition was performed in double crucibles, both porcelain in experiments 1 and 2, the inner one of platinum in the rest of the series. Weights and results as follows:

Cd.	CdO.		Atomic weight of Cd.
1.26142	1.44144		112.12
0.99785	1.40135		112.04
		Mean,	112.08
1.11321	1.27247		111.84
1.02412	1.17054		111.91
2.80966	3.21152		111.87
		Mean,	111.87

In this case additional experiments were made to discover the sources of error, leading to corrections which bring the results near to those found in the chloride and bromide series. Each of the methods is quite fully discussed, and the sources of error are noted. With $O = 16$, 112.39 seems to be a close approximation to the true atomic weight of cadmium.

Molybdenum.—Seubert and Pollard,[1] by two distinct methods, have redetermined the atomic weight of this element. First, melybdenum trioxide was dissolved, in weighed quantities, in a standard solution of caustic soda. The excess of soda was then measured by titration with standard sulphuric acid and lime water. In another set of experiments the volumetric value of the caustic soda had been estimated with standard hydrochloric acid while the last compound had also been determined gravimetrically in terms of silver chloride. Hence the data, all considered together, give from their true end terms, the ratio $MoO_3 : 2AgCl$, although in a very indirect manner; and for this indirection the authors give good reasons. The weights and results, considering only the end terms, are as follows:

MoO_3.	AgCl.		Atomic weight of Mo.
3.6002	7.1709		95.734
3.5925	7.1569		95.708
3.7311	7.4304		95.757
3.8668	7.7011		95.749
3.9361	7.8407		95.720
3.8986	7.7649		95.740
3.9630	7.8941		95.723
3.9554	7.8806		95.694
3.9147	7.7999		95.686
3.8543	7.6767		95.740
3.9367	7.8437		95.688
		Mean,	95.722

[1] *Ztschr. anorg. Chem.*, 8, 434. Calculations on the basis of $O = 15.96$.

Reduced to vacuum standards this becomes Mo = 95.729. With O = 16, Mo = 95.969; and with O = 15.88, Mo = 95.249.

Another series of determinations, in confirmation of the first, was made by the old method of reducing molybdenum troxide in hydrogen. The weight and results are subjoined:

MoO_3.	Mo.	Atomic weight of Mo.
1.8033	1.2021	95.736
1.7345	1.1564	95.777
3.9413	2.6275	95.756
1.5241	1.0160	95.741
4.0533	2.7027	95.813
	Mean,	95.765

Reduced to vacuum, Mo = 95.735, a value very close to the other. When O = 16, the atomic weight of molybdenum is very near the even number 96.

Tellurium.—The determinations of atomic weight by Staudenmeier[1] all start our from telluric acid, $H_2TeO_4.2_2HO$, which had been purified by repeated crystallization. Two essentially different methods were adopted. First, telluric acid was dehydrated, and reduced to TeO_2 by heating. Secondly telluric acid was reduced by heating in hydrogen to metallic tellurium, finely divided silver being mixed with the acid to retain the tellurium by preventing volatilization. In four experiments, TeO_2 was reduced to Te in the same manner. The weights and results may be classified as follows, for convenience of comparison:

TeO_2 : Te.

TeO_2.	Loss on reduction.	Atomic weight of Te.
0.9171	0.1839	127.6
1.9721	0.3951	127.7
2.4115	0.4835	127.6
1.0172	0.2041	127.5

TELLURIC ACID : TeO_2.

Telluric acid.	Loss.	Atomic weight of Te.
1.7218	0.5260	127.2
2.8402	0.8676	127.1
4.0998	1.2528	127.1
3.0916	0.9450	127.05
1.1138	0.3405	127.0
4.9843	1.5236	127.05
4.6716	1.4278	127.1

[1] *Ztschr. anorg. Chem.*, 10, 189. Calculations based upon O = 16 and H = 1.0032.

TELLURIC ACID: TE.

Telluric acid.	Loss.	Atomic weight of Te.
1.2299	0.5471	127.3
1.0175	0.4526	127.3
2.5946	1.1549	127.2

There is a good discussion in the paper as to the possible causes of error in these determinations, and also concerning the place of tellurium in the periodic system. Staudenmeier upholds the homogeneity of tellurium as an element, as against the supposition that it is a mixture.

Some years ago Brauner, in an elaborate paper upon tellurium, sought to show that the ordinary element was a mixture of true tellurium with a higher homologue of atomic weight 214. He now[1] concludes that this is very improbable, and suggests that tellurium may contain a homologue of argon, of atomic weight 130. For this supposition no evidence is given apart from the abnormality of the atomic weight, which should fall below that of iodine.

Yttrium.—The atomic weight of this metal has been redetermined by Jones,[2] who starts out with material purified by Rowland's process, that is, by precipitation with potassium ferrocyanide. First, oxide was converted into sulphate; and secondly, sulphate was transformed to oxide by calcination. The weights and results were as follows:

FIRST METHOD.

Y_2O_3.	$Y_2(SO_4)_3$.	Atomic weight of Y.
0.2415	0.4984	88.89
0.4112	0.8485	88.92
0.2238	0.4617	88.97
0.3334	0.6879	88.94
0.3408	0.7033	88.90
0.3418	0.7049	89.05
0.2810	0.5798	88.94
0.3718	0.7803	88.89
0.4379	0.9032	89.02
0.4798	0.9901	88.91
	Mean,	88.94

[1] *J. Chem. Soc.*, 67, 549.
[2] *Am. Chem. J.*, 17, 154. Calculations made with O = 16, and S = 32.06.

SECOND METHOD.

$Y_2(SO_4)_3$.	Y_2O_3.	Atomic weight of Y.
0.5906	0.2862	88.91
0.4918	0.2383	88.89
0.5579	0.2705	89.03
0.6430	0.3117	88.99
0.6953	0.3369	88.89
1.4192	0.6880	88.99
0.8307	0.4027	88.99
0.7980	0.3869	89.02
0.8538	0.4139	88.99
1.1890	0.5763	88.96
	Mean,	88.97

These determinations are probably the best hitherto made, although they have been briefly criticized by Delafontaine,[1] who prefers the lower value obtained by himself, $Y = 87.3$. Delafontaine reaffirms the existence of phillipium, and regards gadolinium as identical with decipium. Jones,[2] in a brief rejoinder, defends his own work, and urges that Delafontaine has failed to show wherein it is defective.

The Cerite Earths.—Papers upon this subject have been published during the year by Schutzenberger and by Brauner. In his first commnnication, Schutzenberger[3] deals with cerium, which had been freed from lanthanum and "didymium" by fusion of the mixed nitrates with saltpeter. The yellowish-white cerium oxide was converted into cerium suiphate, which was dried at 440°. In this salt, with special precautions, the sulphuric acid was estimated by precipitation with barium chloride. One hundred parts of cerium sulphate gave 123.30 of barium sulphate. Hence, Ce = 139.45, according to Schutzenberger's calculations. Recomputing, with

$$O = 16,\ S = 32.07, \text{ and } Ba = 137.43,$$
$$Ce = 139.96.$$

In a second paper,[4] Schutzenberger describes the results obtained by the fractionation of cerium sulphate. Preparations were thus secured giving oxides of various colors, such as canary yellow, yellowish rose, reddish, and brownish red. These,

[1] *Chem. News*, 71, 243.
[2] *Chem. News*, 71, 305.
[3] *Compt. rend.*, 120, 663.
[4] *Compt. rend.*, 120, 962.

by the synthesis of the sulphates, the barium sulphate method, etc., gave varying values for cerium ranging from 135.7 up to 143.3. Schutzenberger concludes that the cerium sesquioxide from cerite contains small quantities of another earth of lower atomic weight. In a third paper[1] he continues the investigation with the other cerite earths. For the didymiums he finds a range in atomic weight from 137.5 to 143.5, approximately.

Brauner's paper[2] is partly a reclamation of priority over Schutzenberger, and partly a preliminary statement of new results. In his earlier work he found that cerium oxide was a mixture of two earths: one white, the other flesh color with a tinge of orange, and atomic weights for the contained metal of 140.2 and 145.72, respectively. In his later research Brauner fractionates his material by several methods. One constituent obtained from cerium oxide is a dark salmon-colored earth, the oxide of a metal which he calls "meta-cerium." The other constituent he calls cerium. Pure cerium oxalate by Gibbs' permanganate method gave 29.506 and 29.503 per cent. of cerium sesquioxide with 46.934 per cent. of cerium dioxide. Hence, Ce = 139.91, or, with a slight correction, Ce = 140.01. This is not far from Schutzenberger's value.

Helium and Argon.—The true atomic weights of these remarkable gases are still in doubt, and so far can only be inferred from their specific gravities. For argon, the discoverers, Rayleigh and Ramsay,[3] give various determinations of density, ranging (H = 1) from 19.48 to 20.6. The value 19.9 they regard as approximately correct.

For helium, Ramsay[4] gives the density 2.18, while Langlet[5] finds the somewhat lower value 2.00.

From one set of physical data, both gases appear to be monatomic, but from other considerations they are supposably diatomic. Upon this question, controversy has been most active, and no final settlement has yet been reached. If diatomic, argon and helium have approximately the atomic weights, two

1 *Compt. rend.*, 120, 1143.
2 *Chem. News*, 71, 283.
3 *Phil. Trans.*, 186, 220–223.
4 *J. Chem. Soc.*, 3, 684.
5 *Ztschr. anorg. Chem.*, 10, 289.

and twenty, respectively; if monatomic, these values must be doubled. In either case, helium is an element lying between hydrogen and lithium; but argon is most difficult to classify. With the atomic weight 20, argon fills in the eighth column of the periodic system, between fluorine and sodium; but if it is 40, the position of the gas is anomalous. A slightly lower value would place it between chlorine and potassium, and again in the eighth column of Mendejeff's table, but for the number 40 no opening can be found.

It must be noted that neither gas, so far, has been proved to be absolutely homogeneous; and it is quite possible that both may contain admixtures of other things. This consideration has been repeatedly urged by various writers. If argon is monatomic, a small impurity of greater density, say of an unknown element falling between bromine and rubidium, would account for the abnormality of its atomic weight, and tend towards the reduction of the latter. If the element is diatomic, its classification is easy enough on the basis of existing data. Its resemblances to nitrogen, as regards density, boiling point, difficulty of liquefaction, etc., lead me personally to favor the lower figure for its atomic weight, and the same considerations may apply to helium also. Until further evidence is furnished, therefore, I shall assume the values two and twenty as approximately true for the atomic weights of helium and argon.

Carbon.—Wanklyn,[1] on the basis of his investigations into the composition of hydrocarbons, reiterates his belief that the atomic weight of carbon is not 12, but 6. This question is one which falls rather outside the scope of this report and needs no further discussion here. If Wanklyn's contention is sustained, the value assigned to carbon in the table at the close of this paper, should be divided by two.

In the following table of atomic weights, the values are given according to both standards, $H = 1$ and $O = 16$. Many of the figures are the results of new and complete recalculations from all available data, made in the preparation of a new edition of my "Recalculation of the Atomic Weights." This work is now well under way, and it will probably be completed during 1896:

[1] *Chem. News*. 72, 164. See also *Phil. Mag*., August, *1895*. Also the reports of this committee for 1893 and 1894.

	H = 1.	O = 16.
Aluminum	26.91	27.11
Antimony	119.52	120.43
Argon	?	?
Arsenic	74.52	75.09
Barium	136.40	137.43
Bismuth	206.54	208.11
Boron	10.86	10.95
Bromine	79.34	79.95
Cadmium	111.08	111.93
Cesium	131.89	132.89
Calcium	39.78	40.08
Carbon	11.92	12.01
Cerium	139.1	140.2
Chlorine	35.18	35.45
Chromium	51.74	52.14
Cobalt	58.49	58.93
Columbian	93.3	94.0
Copper	63.12	63.60
Erbium	165.0	166.3
Fluorine	18.89	19.03
Gadolinium	154.9	156.1
Gallium	68.5	69.0
Germanium	71.75	72.3
Glucinum	9.01	9.08
Gold	195.74	197.24
Helium	?	?
Hydrogen	1.00	1.008
Indium	112.8	113.7
Iodine	125.89	126.85
Iridium	191.66	193.12
Iron	55.60	56.02
Lanthanum	137.6	138.6
Lead	205.36	206.92
Lithium	6.97	7.03
Magnesium	24.11	24.29
Manganese	54.57	54.99
Mercury	198.5	200.0
Molybdenum	95.26	95.98
Neodymium	139.4	140.5
Nickel	58.24	58.69
Nitrogen	13.94	14.04
Osmium	189.55	190.99
Oxygen	15.879	16.00
Palladium	105.56	106.36
Phosphorus	30.79	31.02

Platinum	193.41	194.89
Potassium	38.82	39.11
Praseodymium	142.4	143.5
Rhodium	102.23	103.01
Rubidium	84.78	85.43
Ruthenium	100.91	101.68
Samarium	148.9	150.0
Scandium	43.7	44.0
Selenium	78.4	79.0
Silicon	28.18	28.40
Silver	107.11	107.92
Sodium	22.88	23.05
Strontium	86.95	87.61
Sulphur	31.83	32.07
Tantalum	181.2	182.6
Tellurium	126.1 ?	127.0?
Terbium	158.8	160.0
Thallium	202.60	204.15
Thorium	230.87	232.63
Thulium	169.4	170.7
Tin	118.15	119.05
Titanium	47.79	48.15
Tungsten	183.44	184.84
Uranium	237.77	239.59
Vanadium	50.99	51.38
Ytterbium	171.7	173.0
Yttrium	88.28	88.95
Zinc	64.91	65.41
Zirconium	89.9	90.6

COMPOSITION OF WOOD GUM.

BY S. W. JOHNSON.

Received January 20, 1896

SINCE 1879, when Thomsen published his investigation "Wood Gum," the writer has, from time to time, opportunity offered, employed several of the chemists of Connecticut Agricultural Experiment Station in work upon alkali-soluble carbohydrates of maize cobs, birch wood vegetable ivory. This work has necessarily been subject to quent and prolonged interruptions, and for that reason the p lication of conclusive results has been greatly delayed.

Wood gum, which is abundantly extracted from the wood deciduous trees by cold, weak (two to ten per cent.) solution

sodium or potassium hydroxide, and thrown down therefrom by neutralization and by alcohol, has been analyzed by Thomsen, Koch, Schuppe and by Wheeler and Tollens.[1]

With exception of Schuppe, all these investigators obtained results on the whole agreeing fairly with the formula $C_6H_{10}O_5$.

Schuppe's analyses mostly gave higher figures for carbon and hydrogen.

Xylan.—When it was shown by Wheeler and Tollens that xylose, the sugar first described by Koch, and obtained by him, from the products of the hydrolysis of wood gum, has the formula $C_5H_{10}O_5$, it became extremely probable that the corresponding anhydride, now designated xylan, has the composition $C_5H_8O_4$.

Analyses made in this laboratory in 1885 demonstrated that the cobs of Indian corn yield to five or ten per cent. potassium hydroxide solution, a body, which, precipitated by alcohol, acidulated with hydrochloric acid, suitably washed and thoroughly dried, has in fact the composition proper to pure xylan.

In 1880 xylan was thus prepared under my direction by Dr. Jenkins, as follows: Ground maize cob was digested for twenty-four hours with frequent agitation in a mixture of one volume of concentrated ammonia with seven volumes of water, the residue was washed on filters to remove all ammonia and digested forty-eight hours with seven per cent. caustic soda solution. The filtered extract was mixed with twice its volume of ninety-three per cent. alcohol. The precipitate was washed until the washings were neutral to test papers, then was stirred up with dilute hydrochloric acid, again washed with dilute alcohol until neutral and thereupon was further treated with absolute alcohol and ether and dried over sulphuric acid. About twenty-five per cent. of white, easily powdered material were thus obtained, which answered to Thomsen's description of wood gum.

It was not made blue by iodine solution. Agitated with pure water at common temperatures for a considerable time, it was taken up to the extent of 0.14 per cent., giving a neutral solution. Boiled for six hours with water, a neutral solution resulted, which contained 0.44 per cent. of dissolved substance that very slightly reduced Fehling's solution. The solution in hot water was unaf-

[1] *Ann. Chem.* (Liebig). 254, 320.

fected by addition of normal lead acetate, but with basic lead acetate gave a heavy flocculent precipitate. Our earlier analyses of this substance gave varying results, due, it may be, partly to impurities, but doubtless largely attributable to its avidity for moisture and the difficulty of drying it completely or of holding it at a constant moisture content.

We could obtain no accordant analyses except by weighing off in quick succession several portions of the air-dry substance that had been fully exposed to air and was neither gaining nor losing moisture, determining carbon and hydrogen in some of these portions and moisture in others, with such precautions as to preclude change of water content.

Hygroscopic water we determined most satisfactorily by drying *in vacuo* at 110°–112°C. For this purpose the substance was contained in a stout glass tube about three cm. wide and ten cm. long, sealed off round at the base and narrowed above to a neck two cm. wide. This was connected by a perforated cork with a water pump, giving a vacuum equal to twenty-eight to twenty-nine and one-half cm. of mercury column, and was heated by placing within a close fitting vertical well, whose sides and bottom were surrounded by boiling aqueous solution of sodium nitrate contained in a closed copper box, the vapor from which was constantly returned by means of an efficient condenser. The glass drying tube, well corked, was counterpoised on the balance by a similar corked tube, and suitable precautions were used to avoid or compensate any changes of moisture of glass or corks.

Recurring to the already published statements, we note that the chemists whose analyses gave results mostly agreeing fairly with the formula $C_6H_{10}O_5$ are silent (in the accounts I have been able to refer to) as to their mode of drying, so Thomsen and Koch, or as in case of Wheeler and Tollens, analyzed "substance that had been dried over sulphuric acid and warmed for some hours at 97° in a water oven."

Mr. Winton, in this laboratory, found that two samples of finely subdivided air-dry wood gum from maize cobs required six days exposure to concentrated aud recently boiled oil of vitriol to come to constant weight, with loss of 8.10 per cent. and

8.11 per cent. and thus dried further lost in three and one-half hours at 100° in a current of dried hydrogen in one case 0.67 per cent., and in another 1.83 per cent., and on further heating in hydrogen for two hours at 120°, lost 0.07 and 0.25 per cent. respectively.

But while it may not be difficult to bring wood gum nearly to complete dryness in the water oven, it is not easy to weigh off, transfer to a combustion tube and burn this dried substance without its taking up sufficient moisture to vitiate an analysis, especially when the atmosphere is humid.

In 1880, Dr. Jenkins, following the methods then in use in this laboratory, made his first analyses of air-dry xylan, determining water by prolonged drying in a water oven. In three combustions he obtained, reckoned on dry matter, 45.25, 45.48 and 45.72 per cent. of carbon respectively. His hydrogen determinations, however, were more irregular, *viz.*: 6.37, 7.35 and 5.90 per cent.

Dr. Jenkins next imperfectly dried his stock of xylan at 100° and weighed off the portions for analysis as required. In four combustions, reckoned ash free, carbon ranged from 44.34 to 45.20 per cent., and hydrogen from 5.92 to 6.01. His averages were: carbon, 44.81; hydrogen, 5.96. These results are quite like those from which Thomsen, Koch, and Wheeler and Tollens deduced the formula $C_6H_{10}O_5$.

Subsequently in 1883, Mr. (now Professor) Milton Whitney, devoted considerable time to analyses of various preparation of wood gum, sometimes using air-dry material, at others substance dried at 100°, but without reaching altogether satisfactory results.

Finally, after I, with Mr. Winton's aid, had accurately ascertained the conditions for completely desiccating this substance and the precautions needful in handling it, it became easy to fix its composition.

In 1885 Dr. Osborne made analyses of a sample of wood gum prepared by Mr. Whitney from corn cobs, being a first fraction thrown down by adding about one-half the amount of alcohol needful for complete precipitation of the soda-lye extract, and otherwise treated as before described. About two grams of this xylan required in one case near six hours heating at 112° in a

vacuum maintained at 29.0 to 29.5 inches mercury, and in another case when the vacuum ranged from 28.5 to 28.0 inches, needed nine hours heating at 112° for reaching constant weights. In either case the loss was 13.51 per cent., and further heating for three hours occassioned no change either in the weight or color of the substance.

Dr. Osborne's combustions of air-dry substance furnished results as follows:

	I.	II.	III.	Average.
Carbon	39.12	39.10	39.06	39.09
Hydrogen	6.81	6.65	6.73	6.73
Ash	0.59	0.66	0.59	0.61
Moisture	....	....	....	13.51

The above average reckoned on dry and ash-free substance is:

		Calculated for $C_5H_8O_4$.
Carbon	45.51	45.45
Hydrogen	6.09	6.16
Oxygen	48.40	48.49
	100.00	100.00

In another similar preparation Dr. Jenkins demonstrated the absence of nitrogen by soda lime combustion.

In two other preparations the ash contents were found to be respectively 0.23 and 1.73 per cent.

At my request Mr. E. B. Hurlburt has lately hydrolyzed corn cob xylan prepared in 1880 and obtained a syrup which, after seeding with a little pure xylose,[1] in a few days, nearly solidified to a mass of crystals that when washed with alcohol and dried, melted at 153° C.

It thus appears that the cobs of Indian corn yield very pure xylan, $C_5H_8O_4$.

It is also probable that many of the analyses of wood gum hitherto published, those of Schuppe possibly excepted, were made on imperfectly dried material, and for that reason mainly, gave results leading to the incorrect formula $C_6H_{10}O_5$.

Birch Wood Gum.—Preparations obtained from the wood of the American white, or gray birch, *Betula alba*, differ in compo-

[1] Kindly supplied for this purpose by Prof. W. E. Stone, who was the first to announce the preparation of xylose from maize cobs.

sition from the xylan of maize cob. Dr. Osborne found in the air-dry substance of one sample:

	I.	II.	Average.
Carbon	42.69	42.49	42.59
Hydrogen	6.65	6.59	6.62
Ash	0.65	0.64	0.65
Moisture	....	....	9.84

Moisture was determined by drying *in vacuo* at 112° C. Constant weight was obtained in one determination in six hours with 29.5 inches of mercury in manometer, the loss being 10.26 per cent., and in another in twelve hours with twenty-eight inches of mercury, the loss being 9.42 per cent.

The average results reckoned on substance free from moisture and ash are:

		Calculated for $C_4H_6O_3$.
Carbon	47.58	47.06
Hydrogen	6.17	5.88
Oxygen	46.25	47.06

These figures for carbon are two per cent. higher than those belonging to the pentosans, and come nearer the composition of a tetrosan.

The birch wood gum, when hydrolyzed, yields a syrup from which, on long standing, or by fractioning with alcohol, a very small proportion of crystals may be separated, which do not appear to be increased in quantity by "seeding" with crystallized xylose.

The further study of birch wood gum and the products of its hydrolysis is reserved.

Mannan.—When the sugar obtained by Reiss[1] from vegetable ivory, the fruit of *Phytelephas*, as the results of hydrolysis, was shown by E. Fischer to be mannose, it became evident that the substance yielding this sugar is a carbohydrate of composition corresponding to the formula $C_6H_{10}O_5$.

According to Reiss,[2] vegetable ivory yields near seven and five-tenths per cent. of a water-soluble carbohydrate, which in the dry state is a yellowish brown gummy mass, having left-handed polarization, readily hydrolyzed and then yielding the

[1] *Ber. d. Chem. Ges.*, 22, 609.
[2] Landwirthschaftliche Jahrbücher, 18, 745, *1889*.

sugar mannose. The vegetable ivory also contains or yields, according to Reiss, a carbohydrate in large proportion, which he prepared as a white amorphous powder by digesting vegetable ivory shavings with an equal weight of seventy per cent. sulphuric acid for twenty-four hours, then adding to the mixture its weight of water, filtering, adding a little alcohol to throw down impurities, and lastly precipitating with mixed alcohol and ether, washing and drying the product. This substance, which Reiss found to swell and partially dissolve in water, and to be laevorotatory and to reduce Fehling's solution, was termed by him seminin and by Tollens[1] paramannan. It yielded mannose on hydrolysis, but its composition, so far as I am aware, has not been determined.

Several investigators have inferred the existence of mannan in seeds of coffee, date, nux vomica, *Diospyros*, cocoanut, and pine wood, etc., from the formation of an insoluble hydrazone in the products of the hydrolysis of these materials, but only Reiss, I believe, has attempted to separate the carbohydrate from the associated substances.

In the year 1880 a quantity of refuse vegetable ivory was sent to this station for examination, with the statement that "it had been used as feed for cattle, which ate it with great relish and fattened upon it."[2]

A "fodder analysis" was accordingly made, the results of which were as follows:

Water (at 100° C.)	18.78
Ash	1.08
Crude fat (ether extract)	0.70
Albuminoids (N × 6.25)	3.37
Crude fiber	7.50
Nitrogen-free extract (by difference)	68.57
	100.00

It was at the same time found that vegetable ivory yields to

[1] Ladenburg's Handwörterbuch, 13, 755.

[2] Loew and Ishii have recently stated that the root of *Conophallus konnjaku*, which is used as human food in Japan, contains mannan, *i. e.*, yields mannosehydrazone in considerable quantity. (Versuchsstationen, 45, 435.) Salep mucilage, formerly used as food for invalids, also very probably contains mannan or a mannocellulose. (Gans and Tollens: *Ann. Chem.*, (Liebig), 249, 256.)

soda lye a large proportion of substance resembling "wood gum," and a number of preparations were made in 1880 by Dr. Armsby, and in 1883 by Mr. (now Professor) Milton Whitney.

Mr. Whitney also analyzed six of these preparations. His mode of drying was long exposure to concentrated sulphuric acid and subsequent heating for one hour in the water oven.

The results of these analyses were not altogether uniform, but either by excluding extremes or taking the average they fairly agreed with the formula $4(C_6H_{10}O_5)\ H_2O$, which requires two and seven-tenths per cent. of hydrate water. This water, however, was doubtless merely hygroscopic.

After having ascertained the precise conditions for determining moisture in various specimens of wood gum, I requested Dr. Osborne in 1885 to analyze two of Dr. Armsby's vegetable ivory preparations then remaining. To determine moisture the air-dry material was heated *in vacuo* (28.0 to 29.5 inches of mercury) at 112° C. for eight to nine hours to constant weight. In one case the substance was further heated for three hours without change in weight or appearance.

The combustions were made on portions of the same air-dry substance as served for estimating moisture.

The following are Dr. Osborne's results:

SAMPLE B. I. 2, AIR-DRY.

	I.	II.	III.	IV.	Average.
Carbon	....	....	40.08	40.17	40.13
Hydrogen	....	....	6.82	6.82	6.82
Ash	....	....	0.10	0.16	0.13
Moisture	9.59	9.65	....	....	9.62

SAMPLE B. II. 1, AIR-DRY.

	I.	II.	III.	IV.	Average.
Carbon	....	....	39.14	39.19	39.17
Hydrogen	....	....	6.92	6.90	6.91
Ash	....	....	trace	trace	trace
Moisture	10.88	10.88	....	....	10.88

The dry ash-free mannan has accordingly the subjoined composition:

	B. I. 2.	B. II. 1.	Calculated for $C_6H_{10}O_5$.
Carbon	44.46	43.95	44.44
Hydrogen	6.37	6.39	6.17
Oxygen	49.17	49.66	49.38
	100.00	100.00	100.00

The mannan of vegetable ivory may be separated in fractions by adding alcohol to its solution in sodium hydroxide.

Armsby's preparation B. I. 2 and B. II. 1 were obtained as follows: One kilo of vegetable ivory turnings was digested for twenty-four hours in a mixture of 800 cc. concentrated ammonia and five and a half liters of water and washed with water until ammonia was removed. The residue was digested twenty-four hours in a solution of 800 grams potassium hydroxide in eight liters of water and filtered, giving a first extract B. I. The undissolved substance was then treated for twenty-four hours with a solution of 480 grams potassium hydroxide in six liters of water and filtered. The second extract was marked B. II.

The potash extract B. I. was mixed with about three-sixteenths of its bulb of ninety-three per cent. alcohol, and allowed to stand an hour; the turbid liquid was separated from the precipitate by decantation and filtration. This first precipitate was B. I. 1. The filtrate therefrom was completely precipitated by its own volume of alcohol, and the second precipitate was B. I. 2, whose analyses correspond so closely to $C_6H_{10}O_5$.

The soda extract B. II. with rather more than one-fourth its bulk of alcohol gave B. II. 1, (containing five-tenths per cent. less carbon than B. I. 2.), and the filtrate therefrom with excess of alcohol yielded a second small precipitate B. II. 2.

These precipitations, after removing mother liquors, were washed with sixty-six per cent. alcohol until nearly neutral, then digested with excess of dilute hydrochloric acid for a day and finally washed out completely with sixty-six per cent., eighty per cent., and absolute alcohol and with ether in succession.

It thus appears that vegetable ivory may yield to dilute caustic alkali solutions a nearly or entirely pure mannan, and that this body is probably accompanied with an alkali-soluble substance of lower carbon content.

METHOD FOR THE DETERMINATION OF CARBON IN STEEL.

BY ANDREW A. BLAIR.

Received January 14, 1896.

THE method given below for the determination of carbon in steel is generally used in the steel works laboratories in the Eastern part of France, and I am indebted for the details to Monsieur H. A. Brustlein of the Aciéries d'Unieux at whose words and at those of the Aciéries de la Marine at Saint Chamond the various improvements in the method have been worked out.

The method was first suggested by Wiborg[1], but was very imperfect in its original form. The greatest improvement was suggested by Monsieur de Nolly of the Laboratory of the Aciéries de la Marine at Saint Chamond and consists in the addition of phosphoric acid to the oxidizing mixture by which the iron is much more rapidly dissolved and the use of a considerable amount of chromic acid is rendered possible without the evolution of a large volume of oxygen gas.

The solutions employed are:

1. A saturated solution of chemically pure cupric sulphate.

2. An aqueous solution of chromic acid (one gram chromic acid to one cc. water).

3. A mixture of sulphuric, phosphoric and chromic acid made up as follows:

Solution of chromic acid (Sol. No. 2)	35 cc.
Water	115 "
Concentrated sulphuric acid	750 "
Phosphoric acid 1.4 sp. gr.	315 "

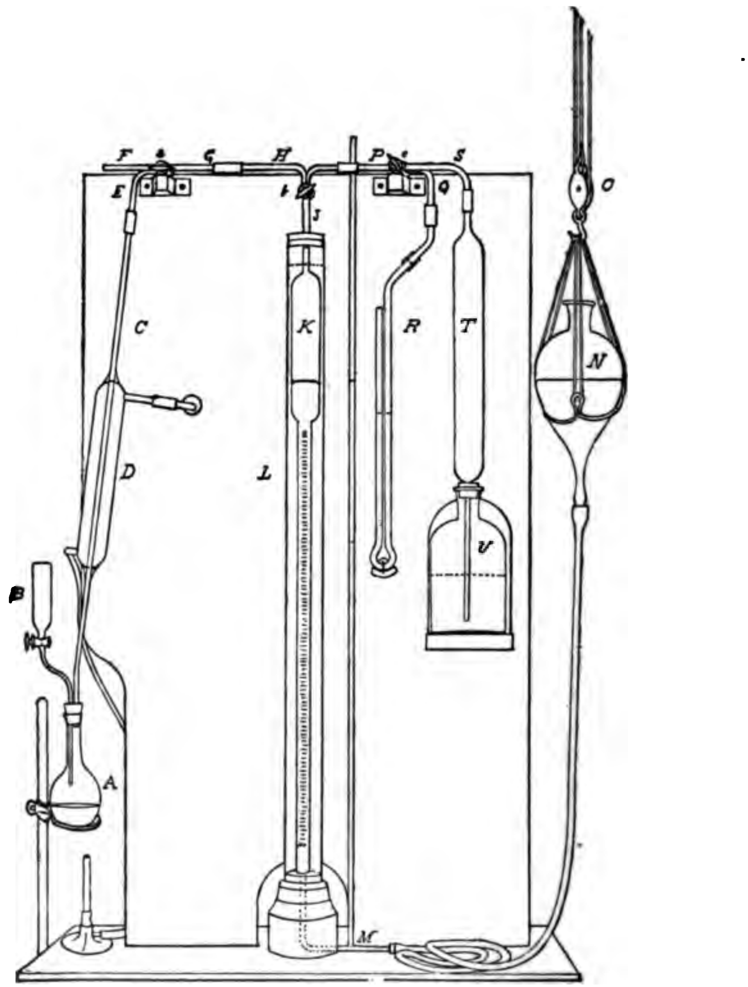
In preparing solution No. 2, add a few cc. of sulphuric acid and heat to boiling to destroy any organic matter that may be present.

In preparing solution No. 3, heat it to boiling also for the same purpose.

The apparatus as shown in the sketch consists of a round bottom Flask *A* of 200 cc. capacity with a long neck. The flask is closed with a rubber stopper with two holes, in one of

[1] Stahl und Eisen, 1882.

which is fitted the glass stopper funnel *B* and in the other the tube *C* enclosed in the condenser *D* through which a stream of water runs during the operation. The tube *C* is connected with



one tube *E* of a three way stop-cock *a*, from which the second tube *F* opens into the air and the third *G* connects with the tube *H* of the three way stop-cock *b*. The second tube *J* from

this stopcock is fused to the burette *K* which is enclosed in the tube *L* containing water. The lower end of the burette connects with a capillary tube *M* which serves as a level tube and is in the form of a T; it is connected with the mercury reservoir *N* which is raised and lowered by the arrangement *O*. The third tube of the stopcock *b* connects with the tube *P* of the stopcock *c*, the second tube *Q* of the stopcock *c* connects with the manometer *R* and the third tube *S* with the pipette *T* which runs into the bottle *U*. The tubes of the stopcocks *b* and *c*, the manometer tube *R*, the level tube *M* and the tubes of the pipette *T* are capillaries. The manometer tube *R* contains water and serves to accurately adjust the levels when taking the reading of the burette *K*. When the manometer is shut off from the burette the approximate level is ascertained by means of the level tube *M*. The tube *F* of the stopcock *a* is used only in exceptional cases: First, when the evolution of gas is insufficient to carry the mercury far enough down the burette *K*, in which case air is drawn through it into the burette; and secondly, when the evolution of gas is so great that it is necessary to make two asborptions in the pipette *T*, in which case the residue from the first absorption is discharged through the tube *F*. The pipette *T* contains a solution of potassium hydroxide of 1.27 sp. gr., and is of about 400 cc. capacity. The bottle *U* is of about one liter capacity. The water in the containing tube *L* serves to keep the gas in the burette at the ordinary temperature of the laboratory. It should be protected from the heat of the burner and flask by a screen.

The operation is conducted as follows:

Connect the pipette *T* by means of the stopcocks *b* and *c* with the burette *K* and, by lowering the mercury reservoir, fill the pipette with the potassium hydroxide solution, close the stopcock *c*, fill the burette *K* with mercury and close the stopcock *b*. Weigh one gram of drillings into the flask *A*, attach it to the apparatus, start the water through the condenser *D*, and connect the flask with the burette *K* by means of the stopcock *a*. Pour fifteen cc. of the cupric sulphate solution No. 1 into the funnel tube *B*, and let it flow into the flask. Allow it to act long enough to form a superficial deposit of copper on the

drillings (one or two minutes is sufficient) then add, through the funnel tube, fifteen cc. of solution No. 2 and 135 cc. of solution No. 3. Heat the solution in the flask and raise it slowly to the boiling point. By means of the reservoir, keep the mercury in the burette and in the tube *M* nearly level. The water condensed in the tube *C* drops back into the flask and keeps the liquid of the same density, while the properly cooled gases pass into the burette.

Allow the flask *A* to cool for about five minutes and then run into it, through the funnel tube *B*, enough water to fill the flask and the tube to the stopcock *a*, thus forcing all the gas into the burette. Close the stopcock *a* and connect the burette by means of the stopcocks *b* and *c* with the manometer *R*, adjust the levels accurately and take the reading of the burette. Then by means of the stopcock *c* connect the burette with the pipette *T* and by raising and lowering the reservoir *N*, pass the gas several times back and fourth to cause the potassium hydroxide to absorb all the carbon dioxide. Finally connect the burette with the manometer tube *R*, adjust the levels and take the reading of the burette.

The burette *K* should contain a few drops of water to insure the saturation of the gases with aqueous vapor. The difference between the two readings is the volume of the carbon dioxide. Observe the readings of the thermometer and barometer and reduce the volume of the carbon dioxide to that which it would occupy in the dry state at 0°C. and 760 mm. pressure.

Multiply the volume of the gas so obtained by 0.0019663 and the result is the weight of the carbon dioxide in grams.

I have constructed the apparatus as here described, and am satisfied that the results obtained by its use when the details of the method are carefully carried out are much more accurate than those arrived at by any other than the combustion method. Blank determinations at Unieux rarely give more than one-tenth cc. or two-tenths cc., when the solutions are properly purified. As results may be obtained in an hour and a half, the method should recommend itself to the chemists of steel works where determinations of carbon are called for in treated and special steels where the color method is inadmissable.

It may be noted here that the use of a condenser and the solutions given above will add to the accuracy of the method in which the carbon dioxide is weighed instead of measured.

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A NEW SAFELY DISTILLATION TUBE FOR RAPID WORK IN NITROGEN DETERMINATIONS.

BY CYRIL G. HOPKINS.
Received December 12, 1895.

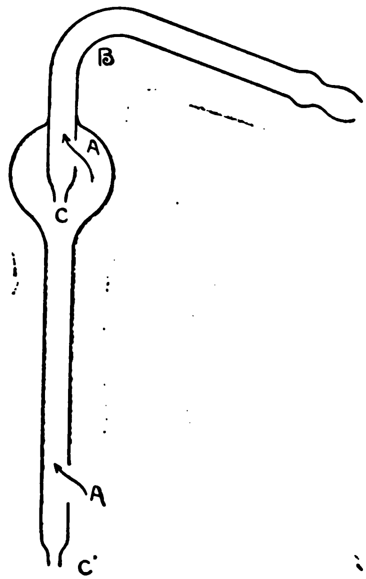
IN doing a large amount of work with fodders and fertilizers, involving several hundred determinations of nitrogen (by the Kjeldahl method), I have observed that the distillation tube (generally known as "Kjeldahl's connecting bulb tube," but doubtless more properly as Reitmeir's distillation tube) is frequently a source of error, due to the fact that it allows fixed alkali to be carried over mechanically. Especially in this the case when the distillation is carried on rapidly, and also when the contents of the distillation flask has a tendency to "bump."

In doing rapid work I have always found it necessary to have the lower end of these tubes reground before they would allow the liquid condensed in the bulb to run back into the distillation flask. Even after this is properly done the lower end of the tube is still open, and when the liquid boils violently or "bumps," small particles of it are often thrown up through the tube into the bulb. Sometimes these particles of strongly alkaline liquid strike the curved tube within the bulb, flow out to the end, and are forced into the tube and over into the condenser by the rapid current of vapor. This action is easily observed when the contents of the distillation flask is highly colored; and I find that the occurrence is familiar to chemists who have had much to do with nitrogen determinations.

I have obtained good results, however, by having the end of the tube within the distillation flask properly ground, and then protected by a larger glass tube, fastened to the distillation tube just below the rubber stopper, by means of a short piece of rubber tubing, and having an opening on the side and a jet at the lower end. This modification gave such good satisfaction that it finally led me to make a new distillation tube in which

not only the tube which passes into the distillation flask, but also the tube within the bulb has an opening on the side and a jet at the end.

The form of this distillation tube and its advantages over the tube in ordinary use will be plainly seen in the accompanying illustration.



The vapor passes in through the side openings A and A', and whatever condenses in the tube below the point B passes back into the distillation flask through the jets C and C'.

The possibility of liquid from the distillation flask being thrown into the tube is avoided, and the current of vapor does not interfere with the return of condensed liquid. The jets C and C' are two mm. inside diameter and they always remain filled with returning liquid when in use. The tubing used in making these distillation tubes is from seven mm. to eight mm. inside diameter. The side openings A and A' should be nearly as large, and the bulb, about five cm. in diameter. The length of the tube below the bulb is twelve cm. and that above the bulb about the same.

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REMARKS ON MR. AUCHY'S PAPER ON THE VOLUMETRIC DETERMINATION OF MANGANESE.

BY GEORGE C. STONE.

Received January 11, 1896.

IN the December number of the Journal of the American Chemical Society there is a paper by Mr. George Auchy on the "Volumetric Determination of Manganese," in which he advocates the use of Volhard's method, in which I heartily agree

[1] Read before the New York Section.

with him, but the method as he describes it, seems to me unneccesarily complicated.

Mr. Auchy criticises Williams' method and refers to the discussion of it which occurrred some years since.[1] At that time I satisfied myself that the method as originally described by Williams was not accurate, but in a modified form I used it for several years with good results until I, too, was treated to the same disagreeable surprise as Mr. Auchy, a member of manganese determinations came very low. On examination I found that this was due to the decomposition of the oxalic acid solution. I then gave up the method and have since used Volhard's with uniformly satisfactory results, except where there are only a few hundredths of a per cent. of manganese present, in which case I found the method of oxidizing by peroxide of lead, reducing by standard arsenious acid and titrating back by permanganate to work well.

Volhard's method, as I have used it, is as follows: The quantity of material taken for analysis should contain between 0.05 and 0.15 grams of manganese. If it is an alloy, dissolve in nitric acid of about 1.10 sp. gr.; if an ore or cinder, dissolve in hydrochloric acid and boil with a little potassium chlorate. In either case use but a small excess of acid. Cool, wash into a half liter flask with cold water and add an emulsion of zinc oxide until the precipitate curdles; the change in the appearance of the precipitate is sharp and distinct. Dilute to the mark, mix thoroughly, pour into a beaker and allow the precipitate to settle. Decant off exactly 100 cc. into a four inch casserole, dilute to about 200 cc., heat nearly to boiling and titrate rapidly with permanganate, one cc. of which should equal 0.001 gram of manganese (about 1.99 grams potassium permanganate in one liter). The greater part of the permanganate should be added at once and the solution very vigorously stirred. For this purpose a glass rod bent to a hook is very convenient, the hook of course being in the solution.

I have made a number of experiments to see if it makes any difference whether nitric, hydrochloric or sulphuric acid is used, and have not found that it does, provided the iron is oxidized. For

[1] Trans. Am. Inst. Min. Eng., 11, 514; 12, 295-449; *Chem. News*, 1883, 176-273.

neutralizing I use commercial zinc oxide, which contains a trifling amount of manganese, but under the conditions in which it is used this apparently does not go into solution. To test this point, I made a number of duplicate analyses, neutralizing one of each pair with zinc oxide and the other with barium carbonate; in all cases the results agreed well. It is not necessary to filter the solution; the iron precipitate settles very rapidly and completely, and if a little of the precipitate goes with the solution, it makes no difference. I think the trouble Mr. Auchy mentions in getting good results with steels low in manganese when a large excess of zinc oxide is used, is due to not having sufficient manganese present, as it is difficult to make a very small precipitate clot together so as to give a clear solution in which the color of the end reaction shows distinctly. I have often tried adding a very large excess of zinc oxide, but have never found it to interfere, provided the manganese was within the limits given above.

The method is very rapid, a determination of manganese in spiegel can easily be made in half an hour; ores usually take a little longer, as they are more difficult to dissolve.

PROBABLE PRODUCTION OF PERMANGANATE BY DIRECT COMBUSTION OF METALLIC MANGANESE.[1]

BY GEORGE C. STONE.

Received January 11, 1896

WHEN casting at a Spiegel furnace, a good deal of iron and manganese is always burned at the tap hole, giving a very hot flame aud clouds of reddish fume, the hotter the furnace and the higher the percentage of manganese in the iron; the more sparks and fume. To protect themselves from these sparks the men often put a sheet iron screen over the run and tap holes. One day some water was accidentally spilled on this screen immediately after casting. It at once took the deep purple color of a permanganate solution; unfortunately the screen was upset and the solution spilled before I could secure any of it for further examination. At the time the furnace was working very hot, making a high grade spiegel and a basic cinder.

DISCUSSION.

Dr. Rosell called attention to the fact that potassium permanganate when heated to a red heat would decompose, and that the

[1] Read before the New York Section.

other permanganates behave in the same way. In fact the permanganates can only be made in the wet way. On the other hand, manganates are generally produced in the dry way, and they will stand a very high temperature.

If, therefore, a substance, after having been heated to the temperature of the blast furnace, would dissolve in pure water with the well known rich purple color of a permanganate solution, it seems almost certain that such a substance could not be a permanganate, but it could be a solution of a ferrate. It is, of course, also possible that the water used to dissolve the substance in question was not pure, but accidentally contained some acid, whereby, on dissolving, the manganate was converted into permanganate.

THE MANUFACTURE OF ACETONE AND OF ACETONE-CHLOROFORM FROM ACETIC ACID.[1]

By Edward R. Squibb.

Received January 25, 1896.

JUST one year ago, January 11th, 1895, the writer read a paper before this Society upon "Improvement in the Manufacture of Acetone," and this paper was published in the Journal for March, 1895, page 187. The improvement claimed consisted in the use of acetic acid, instead of acetates, and in the use of a rotary still for the decomposition. The results given were obtained from a model apparatus on a table.

During the year that has elapsed since that paper was read, a large rotary still, twelve feet in length by two feet in diameter, has been set up, and this has decomposed in 126 hours about 1,700 pounds of absolute acetic acid, giving about ninety per cent. of the theoretical yield of acetone against about eighty per cent. in the small apparatus.

But the patentees of the processes for making acetone from acetates object to the use of this process and apparatus as being in conflict with their patents.

The acetone produced was converted into chloroform by the Watts (Seimerling) proportions of material in an apparatus described by the writer in 1857,[2] and used for many years in making chloroform from alcohol, and this is also objected to.

1 Read before the New York Section, January 10, 1896.

2 *Ephemeris*, 4, [1], 71.

Under these circumstances it seems necessary to find out what has been done in the past upon this important subject, and what may be the relations of past work to the present conditions, and in this it is hoped the society may be interested.

ACETONE.

It is impossible to determine when or where acetone was first made and used.[1] According to the authority last given, after the time of Boerhaave in 1732, "the body was but little investigated until 1805, when Trommsdorff stated that on distilling acetate of potash or soda, a liquid was obtained which stands between alcohol and ether." In 1807 the Brothers Derosne in Paris[2] studied its properties; and in 1809 Chenevix[3] demonstrated that this substance was obtained by the dry distillation of any one of the acetates.

The correct composition of acetone was first given by Liebig[4] and Dumas.[5]

Further investigations by Kane, 1838, and by Chancel, Williamson, Chiozza, Freund, Wanklyn, and others, still more definitely established the sources, character and properties of acetone, and gave it a definite chemical and economic position so that its production or manufacture by the dry distillation of acetates was as well known as the production of alcohol by distillation from fermented sugars, as early as 1848, when Böttger refers to it as a market article in common use. Wackenroder,[6] in 1848, states that since acetone is quoted on the price lists at ten sgr. (Silbergroschen) per ounce, the preparation of chloroform from it is well worth recommending.

In "Handwörterbuch der reinen und angewandten Chemie herausgegeben von Dr. J. Liebig, Dr. J. C. Poggendorff und Dr. Fr. Wöhler—Redigirt von Dr. Hermann Kolbe, Braunschweig," 1842, Vol. II, p. 1018, is the following (translated) statement:

According to Justus Liebig and Pelouze, the best thing to use

[1] See Wurtz' Dictionnaire de Chimie, 1873, 1, 31; Gmelin: Handbook of Chemistry, 1855, 9, 1; Roscoe and Schorlemmer: A Treatise on Chemistry, 1882, 3, [1], 568.

[2] *Ann. de Chim.*, 63, 267

[3] *Ann. der Phys.*, 32, 191.

[4] *Ann. Pharm.*, 1, 223.

[5] *Ann. Chim. Phys.*, 49, 208.

[6] *Archiv. der Pharm.*, 53, 273.

for the preparation of acetone is concentrated acetic acid, which in the state of vapor is conducted through a heated tube of glass, porcelain or iron, which for the sake of increasing surface, is filled with pieces of charcoal, and the products of decomposition are condensed in the usual way. The tube should be heated only to incipient redness; at a higher temperature only empyreumatic oils, combustable gases and charcoal are obtained as the products of the decomposition.

Besides the citations given, the literature on the preparation, properties and reactions of acetone is very copious and definite up to about 1853. After this date the papers published are comparatively few, leading to the inference that the substance had reached a definite position and gone into general use.

In a paper by Prof. Samuel P. Sadtler, Ph.D., "On Recent Improvements in the Methods for the Manufacture of Chloroform," published in *The American Journal of Pharmacy* for July, 1889, p. 321, the following statements are made:

"The old process of manufacture by the action of bleaching powder upon alcohol has given way to what is now termed the 'acetone' process. This is not, however, a new discovery. Liebig, in 1832, in following up his first account of the properties of the newly discovered "chloride of carbon" (chloroform) mentions that it can be gotten in very large quantities by the action of bleaching powder upon 'pyroacetic spirit' (acetone) as well as from alcohol. That alcohol has all this time been preferred to acetone as a material from which to prepare chloroform is due mainly to the fact that only in recent years has acetone been prepared pure in quantity, but also to the erroneous statement of Siemerling, quoted in the works of reference like Watts' Dictionary of Chemistry, that only thirty-three per cent. of chloroform could be gotten from acetone by the action of bleaching powder." . . . "The manufacture of a purer grade of acetone than that then in use for solvent purposes, having been begun in Germany in 1881, on the part of the 'Verein für chemische Industrie,' Liebig's old suggestion for the manufacture of chloroform from acetone was taken up by the 'Verein Chemischer Fabriken,' Mannheim, Germany, in the beginning of 1882, and a year later by the first mentioned company which made the acetone for both."

From these references it will be seen that the reactions involved in the production of acetone, and the constitution, character, properties and reactions of acetone had been long and well known prior to 1848, and that it had been made and utilized on a large scale prior to 1882; and further, that it had been produced both by the dry distillation of acetates, and by the wet distiilation of acetic acid, as a matter of open knowledge and practice.

This condition of the scientific knowledge of an important chemical substance throughout France and Germany—and throughout the scientific world—makes it very certain that the chemical industries, which depend upon such knowledge for their origin and progress in general, but do not publish their processes—availed themselves of this knowledge and of this chemical agent.

In June, 1886, application was filed in the U. S. Patent Office, and two years later, in July, 1888, Letters Patent No. 385, 777 were issued to Gustav Rumpf for the invention of a "New and Useful Improvement in the Manufacture of Acetone," and from the specifications and claims of this patent the following extracts are made:

"In making acetone by dry distillation of acetates, as acetate of lime, it has, before my invention, been thought possible to obtain only less than half the acetone."

"Dr. Herman Hager, in his Handbuch der pharmaceutischen Praxis, published in Berlin in 1882, states under the head of 'Acetone,' 'that it is possible to obtain an average yield from chemically pure acetate of lime of only fifteen per cent. of acetone, while the theoretical yield from chemically pure acetate of lime is thirty-four per cent.'"

"I have discovered that if the acetates are subjected for distillation to a low heat and approximately uniform temperature and the process extended over several hours, the yield of acetone will be greatly increased, and will approach very nearly the theoretical yield of any particular acetate, which in the case of good gray or commercial acetate of lime is about twenty-seven per cent. I have also discovered that in the process of subjecting acetates in a closed vessel to heat applied externally to the vessel

for distilling acetone from the acetates the desired slowness of distillation and uniformity of temperature may be secured by stirring the acetates so that all portions of the mass will be subjected to the heat resulting from direct contact with the bottom of the vessel, and by admitting free steam from time to time into direct contact with the acetates in case of any undesirable rise in temperature within the vessel."

"My invention consists in an improvement in the method of obtaining acetone from acetates by destructive distillation, consisting in subjecting the acetates in a closed vessel to slow destructive distillation at a low and approximately uniform temperature, and it is also well to stir the acetates during such distillation."

The claims are to—

"The improvement in the method of obtaining acetone from an acetate consisting in subjecting the acetate in a closed vessel to slow destructive distillation at a low and approximately uniform temperature."

This first broad claim is based, not upon the chemical reaction which was well known, nor upon the destructive distillation by heat, which was a well known process, but upon an improvement in the apparatus and management by which the yield of acetone was alleged to have been increased. But the evidence upon which the increase is claimed is an erroneous statement quoted from Hager—erroneous because it is hardly practicable through any ordinary degree of want of knowledge and skill to obtain so little as fifteen per cent. of acetone from acetate of lime.

The second claim is to a stirrer in its effects on the process. But a stirrer is a device so common in chemical processes that no such application of it can be considered original or new.

The third claim to the effect of the introduction of steam during the distillation is much better.

The fifth, sixth, seventh and eighth claims are to improvement in the process of purifying the crude acetone by means of lime, dilution and rectification, and these are but the steps common to all such operations.

It is upon this patent that infringement is charged, when it is

simply putting into use the very old process of making acetone by the destructive distillation of acetic acid in a rotary still as described in a paper on "Improvement in the Manufacture of Acetone," read before this New York Section of the American Chemical Society on January 11, 1895, and published in the Journal for March, 1895, p. 187, and in *An Ephemeris of Materia Medica, Pharmacy, Therapeutics and Collateral Information*, Vol. IV, No. 3, p. 1653.

The writer makes acetone by the destructive distillation of the watery vapor of acetic acid in a rotary still, in the presence of barium carbonate or pumice-stone or bone-charcoal, barium carbonate being preferred, because being a very heavy powder, a larger charge of smaller volume can be used.

The patentees claim only acetates as their material, but claim infringement by the use of acetic acid, because acetic acid is made from acetates, and acetates are made from acetic acid; and secondly, claim infringement on the ground that acetate of barium is first formed, and then decomposed in the rotary still, and therefore the process is really not a destructive distillation of acetic acid, but of barium acetate—one of the class of acetates claimed as secured to them by their patent, although in use for this purpose for so many years. That is, it is claimed that an acetate of barium is formed under conditions of temperature in which an acetate of barium cannot exist. Barium acetate decomposes at about 400° to 405° C. by an ordinary pyrometer. Acetic acid is best decomposed at about 500° to 525° C. by the same pyrometer, and yet it is claimed that at 500°C. barium acetate forms momentarily and then is instantly decomposed. That is, it is formed in an atmosphere in which it cannot exist for an instant, and in which acetic acid cannot exist.[1]

[1] Upon this point the patentees were very decided in the statement, based not only on their own experience, but also on the experience of their German correspondents, that if the barium carbonate was replaced by pumice-stone the amount of acetone obtained would be too small to have any commercial importance. This result had been confirmed to them by so many trials that at their suggestion, and in order to satisfy them that their results were not trustworthy, the following experiments were made after the above paper was written, but before it was published.

The large rotary still was emptied and cleaned out by sweeping, scrap-

But, quite apart from this, the chemical reaction by which acetone is produced, whether from acetates or from acetic acid, was well known for more than half a century before the date of this patent. What is really covered by the patent is certain specified and described apparatus and management whereby an improved yield is to be obtained from acetates, and from acetates only, for the apparatus and management are not at all applicable to the use of acetic acid, and are not used either in form or substance.

ACETONE-CHLOROFORM.

The history of acetone-chloroform dates distinctly back to 1832. In the *Annalen der Pharmacie*, *1832*, **21**, 198, Liebig describes the preparation of chloroform in large quantity, from given proportions of hypochlorite of lime, water, and alcohol, and he says the yield will be equal in weight to the alcohol used. He then goes on to say that chloroform may also be obtained in large quantity by treating acetone with hypochlorite of lime under the same conditions.

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ing, and finally by sponging with water until it was quite free from any appreciable quantity of barium salt. It was then closed and run empty with a continuous feed of acetic acid for periods of three hours each, at the following temperatures, the rate of feeding, and the assaying for acid and acetone being approximate only, and only trustworthy by averaging.

At 300° C. 22.3 pounds of absolute acid was run in and
19.5 " " " " " received without any acetone or any evidence of decomposition of the acid, the 2.8 pounds of acid not accounted for being the normal charge of the apparatus.

At 350° C. 38.3 pounds of absolute acid was run in and
38.1 " " " " came through with no signs of any decomposition,—no acetone.

At 400° C. 36.1 pounds of absolute acid was run in and
29.9 " " " " " received undecomposed, leaving
6.2 " " " " decomposed, and this decomposed acid gave 97 per cent. of the acetone required by theory.

At 450° C. 35.1 pounds of absolute acid was run in and
18.5 " " " " " received undecomposed, leaving
16.6 " " " " decomposed, which apparently gave 112 per cent. of the acetone required by theory.

At 500° C. 41.4 pounds of absolute acid was fed in and
10.8 " " " " " received undecomposed, leaving
30.6 " " " " decomposed, which apparently gave 104 per cent. of the acetone required by theory.

At 550° C. 40.4 pounds of absolute acid was fed in and
5.1 " " " " " received undecomposed, leaving
35.3 " " " " decomposed, which apparently gave 82 per cent. of the acetone required by theory.

Liebig does not give the yield from acetone, but after giving the yield from alcohol as being equal in weight to the alcohol used, he says it is obtained in large quantity from acetone.

In 1835 Dumas and Peligot[1] state that when a solution of hypochlorite of lime is distilled with wood spirit there is obtained, as a matter of fact, some ordinary chloroform. The experiment is as easy as with alcohol or acetone.

Then a run of twenty-four hours was made at the last temperature, 550° C. to give opportunity for closer determinations of results.

321 pounds of absolute acid was fed in and
57.3 " " " " " received undecomposed, leaving
263.7 " " " " decomposed, which apparently gave 97 per cent. of the acetone required by theory.

The still was then opened, charged with 130 pounds of coarsely ground pumice-stone, and a parallel series of experiments made.

At 300° C. 41.8 pounds of absolute acid was fed in and
39.1 " " " " " received undecomposed, leaving
2.7 " " " " decomposed, which apparently gave 33.5 per cent. of the acetone required by theory.

At 350° C. 39.6 pounds of absolute acid was fed in and
34.8 " " " " " received undecomposed, leaving
4.8 " " " " decomposed, which apparently gave 87.5 per cent. of the acetone required by theory.

At 400° C. 41.8 pounds of absolute acid was fed in and
28.5 " " " " " received undecomposed, leaving
13.3 " " " " decomposed, which apparently gave 97 per cent. of the acetone required by theory.

At 450° C. 41.8 pounds of absolute acid was fed in and
13.0 " " " " " received undecomposed, leaving
28.8 " " " " decomposed, which apparently gave 95 per cent of the acetone required by theory.

At 500° C. 43.4 pounds of absolute acid was fed in and
8.8 " " " " " received undecomposed, leaving
34.6 " " " " decomposed which apparently gave 96.4 per cent. of the acetone required by theory.

At 550° C. 43.4 pounds of absolute acid was fed in and
7.4 " " " " " received undecomposed, leaving
36.0 " " " " decomposed, which apparently gave 100 per cent. of the acetone required by theory.

Then a run of twenty-four hours was made at the last temperature, 550° C., as a check upon the previous results.

345.5 pounds of absolute acid was fed in and
69.5 " " " " " received undecomposed, leaving
276.0 " " " " decomposed, which apparently gave 104 per cent. of the acetone required by theory.

This last, and three other impossible results are as yet unexplainable, but they may be reasonably charged to the uncertainties in the use of an hydrometer and the iodoform process of assaying.

1 *Ann. Chim. Phys.*, 58, 15.

Liebig in his text-book[1] gives a formula and directions for the manufacture of chloroform from either acetone, alcohol, or wood spirit, and gives to acetone the leading place.

M. Bonnet[2], at a meeting of the Academy, says, "I have obtained in the distillation of equal parts of acetate of lime and hypochlorite of lime, in a stone retort, a very large quantity of chloroform, and far more easily than by the methods of preparation that are known.

Dr. Reich[3] proposed and used hypochlorite of sodium in place of hypochlorite of lime on account of the uneven amount of chlorine in the latter. He distilled together two pounds each of hypochlorite and acetate of sodium and received five to six drams of chloroform and twelve to fourteen ounces of acetone and water. This latter was again distilled with four to six ounces of hypochlorite, and again a considerable amount of chloroform and acetone was received. The last operation was repeated with a new portion of hypochlorite, and then the total amount of chloroform was eight to ten ounces, with still some excess of acetone for future operations.

Acetone when distilled with sodium hypochlorite yields chloroform in the proportion of four ounces of acetone to five to five and one-half ounces of chloroform.

Prof. Böttger[4] distilled together equal quantities of commercial bleaching powder and crystallized sodium acetate and obtained chloroform and acetone. Then he distilled the excess of acetone with a fresh portion of bleaching powder and had "great joy in seeing from this second operation a very considerable quantity of the purest chloroform distill over together with some acetone still undecomposed." The excess of acetone was again distilled with fresh bleaching powder and the process repeated until by three to four distillations all the acetone was used. The yield of chloroform being about four ounces to each pound of bleaching powder.

Chloroform made directly from acetone, which he says is at present, 1848, to be had in the market, is obtained in the propor-

1 Traité de Chimie Organiques, 1, 576.
2 L'Institut, No. 196 Februar, 1837.
3 *Archiv der Pharmacie*, Zweite Reihe, *1848*, 55, 65.
4 Polytechnisches Notizblatt, *1848*, 3, 1.

tion of one ounce and two drams of chloroform from one ounce of acetone.

Still in the year 1848 Prof. Heinrich Wackenroder,[1] one of the editors of the *Achiv*, says in substance: "The great practical interest in chloroform at the present time calls, first of all for a closer examination of the methods for making it. Therefore I have induced Mr. Siemerling to undertake, in my laboratory, some experiments relating to the preparation of chloroform which are in the most recent publications on the subject. Although these experiments have in no respect given the results which were hoped for; it nevertheless seems to be worth while to call attention to them for the sake of the future continuation of the subject."

Then follows the paper of Mr. V. Siemerling, and at page 26: "II. Preparation of Chloroform from Acetone."

"According to the statement of Prof. Böttger, one ounce of acetone, which has been mixed with hypochlorite of lime to a pasty mass, should give one ounce and two drams of chloroform. As this seemed to be an easy and advantageous method of preparation, some experiments were made with acetone procured from the factory of Trommsdorff, in Erfurt, but they did not accord with the statement of Böttger."

"In the first experiment (*a*) thirty grams of acetone were mixed with fifty grams of hypochlorite of lime and fifty grams of water and distilled. The chloroform was separated and rectified with concentrated sulphuric acid. The yellow chloroform thus obtained was again rectified from burnt lime when it had an empyreumatic odor—quantity not given."

In experiment (*b*) thirty grams of acetone, 120 of hypochlorite and enough water to make a pasty mass, were mixed and distilled. It is true much chloroform came over, but there was also much undecomposed acetone as well. It was repeatedly washed with water and rectified over calcium chloride, in which rectification there was a pretty large loss every time, but the number of times is not given. The yield was nine grams.

Experiment (*c*), since in both experiments undecomposed acetone distilled over the quantity (proportion) of hypochlorite was

[1] *Archiv. der Pharmaci.*, 1848, 54, 23.

increased, and thirty grams of acetone to 150 grams of hypochlorite, with water, were mixed to a pasty mass, allowed to stand twenty-four hours, and were then distilled. The product contained much chloroform, but also undecomposed acetone; therefore it was put back into the retort with forty grams of fresh hypochlorite and again distilled. The chloroform thus obtained still contained acetone, from which it was purified by repeated washing with water, and then rectified over calcium chloride. The yield was ten grams of chloroform.

Another experiment (*d*) is given wherein twenty grams of acetone and sixty grams of hypochlorite were distilled together without water, but with unfavorable result, the yield being six grams of chloroform.

The specific gravity of the chloroform obtained from acetone, after repeated rectifications over calcium chloride was only 1.31, and it always contained some acetone; and the largest yield by Böttger's process was one-third of the acetone used. This differs considerably from his statement that one part of acetone yielded one and one-fourth parts of chloroform.

Siemerling then goes on to say, that if we assume with Liebig, that acetone is composed of one atom of acetyl oxide and one atom of methyl oxide, and explain in this way the formation of chloroform, from methyl oxide, it naturally follows that we must get less chloroform than the acetone used.

The sum of the elements of one atom of acetyl oxide $= C_4H_6O$ and one atom of methyl oxide $= C_2H_6O$ is equivalent to two atoms of acetone $= C_6H_{12}O_2$. In thirty grams of acetone there are therefore 11.8 grams of methyl oxide, which, since four atoms of methyl oxide consist of the same elements as two atoms of alcohol, can form 15.1 grams of chloroform, assuming that complete decomposition takes place.

According to the theory, half of the acetone used must be recovered as chloroform; but since in the practical manufacture of chemical products the quality prescribed by theory is never obtained, it should be considered a favorable result when one-third of the acetone used is obtained as chloroform, especially as the experiments were made only on the small scale.

From these experiments, it follows that the preparation of

chloroform from acetone is quite unfit for practical use. Were even the quantity of chloroform stated by Böttger as obtainable from acetone possible, it would have the disadvantage of being freed from acetone with very great difficulty.

The paper of Siemerling, from which the above abstract is made, seems to have received the endorsement of Wackenroder, although it controverts the statements of both Reich and Böttger, and it may be from his high authority as much as from the paper itself that the results seem to have been accepted and quoted by Gmelin,[1] Watts,[2] and other reference authorities, and the influence of the publication seems to have been, so far as the literature of the subject goes, to prevent or obstruct the acetone process for many years. As it was so long and so well-known, manufacturers may have been, and probably were using the process privately, but up to 1881–1883[3] very little information on the subject is found. Still the work and the conclusions of Siemerling must have been known to be grossly erroneous by every one whose interest it became to try them. Calculations would show to anyone that when ordinary acetone and bleaching powder were used the proportions required are about one to ten, or about double the largest proportion of hypochlorite used by Siemerling, and the resulting chloroform should be about double the weight of the acetone used; and many who preceded Siemerling knew better than he how to save and utilize the great excess of acetone, or deficiency of hypochlorite taken.

But the Siemerling results were very faulty and very misleading in other respects. The present writer having learned from all the work of the past on the subject, that any excess of acetone used could be easily recovered and used again, added to this knowledge from his own experience the fact, that, where an excess of acetone was taken, the hypochlorite was more economically and more promptly utilized, and the resulting chloroform was cleaner. Having gained from the Siemerling process this step the writer was prepared to try that proportion and process critically, and he found that, as a table experiment, it was

1 Handbook of Chemistry, Vol. VII, 346.
2 Dictionary of Chemistry, *1883*, I, 918.
3 Sadtler, *Am. J. Pharm., July. 1889*, 321.

quite impracticable by any reasonable degree of mismanagement to obtain so low a result. In two fairly careless trials from thirty grams of ninety-six per cent. acetone the yield of chloroform was twenty-three grams in one case and thirty-two grams in the other, instead of Siemerling's ten grams. In larger trials of his proportions up to 280 pounds of absolute acetone to one cask of 1400 pounds of thirty-three per cent. bleaching powder in one charge the yield was not less than 200 pounds of chloroform, and about 130 pounds of recovered acetone, thus proving conclusively the gravity of the unaccountable errors of the Siemerling work, and showing a basis for the mischief done by this bad work.

Looking back from this later day at the authoritative way in which these mistakes and misstatements of Siemerling were published and quoted, it is easy to see that nothing could be better adapted to obstruct or prevent any increase in the general production of acetone-chloroform, and to confine its productions to those manufacturers who were using the process secretly.

One of the definite evil consequences of this Siemerling paper was the adoption of its erroneous results as the basis of the following patent.

On June 23, 1886, Gustav Rumpf applied for a patent, and on July 5th, 1888, patent No. 383,992 was issued to him for the invention of " A New and Useful Improvement in the Manufacture of Chlroform from Acetone," of which the following is a specification : " The essential feature of this invention is based on the discovery that acetone when treated in the proper way with a hypochlorite—for example chloride of lime—will yield a larger quantity of chloroform than has been heretofore known. Watts, in his Dictionary of Chemistry, edition of 1883, **1**, 918, says that the manufacture of chloroform from acetone cannot usefully be carried out, not only because the price of acetone is too high, but particularly because acetone yields about thirty-three per cent. of its own weight of chloroform when it is treated with chloride of lime. Watts distilled thirty grams of acetone with 150 grams of chloride of lime, and rectified the watery distillate with forty grams of chloride of lime. I have discovered a method whereby it is possible to obtain a yield of chloroform from ace-

tone very much greater than that obtained by Watts. I have found that the reaction may be made to take place in such a way that one equivalent of acetone will yield one equivalent of chloroform by volume, or about 180 per cent. by weight, and the advantages of my invention may be secured in a greater or less degree by properly employing with about fifty-eight pounds of acetone more than 300 pounds of good chloride of lime. The best results and greatest yield of chloroform can, as I have found, be obtained by the use of, say, fifty-eight pounds of acetone to at least 600 pounds of a good chloride of lime containing about thirty-five per cent. of available chlorine, and in proportion if the chloride of lime is poorer. The yield of chloroform will then be from 150 per cent. to 180 per cent. of the weight of the acetone employed instead of about thirty-three per cent.

Then follow claims for invention of diluting the acetone and of introducing it periodically during the process—of introducing it below the surface of the solution in the still—of the use of a mechanical stirrer, and of the use of a still and condenser which are described and figured.

The basis upon which this patent rests, for its reason to be, is the quotation from Watts' Dictionary. Watts quotes the process from *Gmelin's Handbook*, and Gmelin quotes it from *Siemerling's Paper* in the *Archiv der Pharmacie, 1848*, **54**, 26. Now, as the paper and quotations are grossly erroneous, and as writers of preceding papers publish results that approximate those of the patent, it might reasonably be asked what is the value of the patent. But the present writer, while intending to make acetone-chloroform, very earnestly desires to avoid all question in regard to the validity of this patent, and therefore uses the Watts (Siemerling) process, which is outside the limit claimed by the patent, with an entirely different apparatus and management described by him in 1857, and republished in *Ephemeris*, **4**, [1] 71.

It is proposed to use charges of 280 pounds of absolute acetone to 1,400 pounds of thirty-five per cent. bleaching powder, one to five—to pass the resulting chloroform through scrubbers, then distil it through water, then distil it from a small portion of bleaching powder, then pass it through sulphuric acid scrubbers,

and finally rectify it in three fractions, the large middle fraction being accepted, and the others being worked over.

A part of the great excess of acetone taken in the one to five proportion is recovered by continuing the distillation after the chloroform is all over. Another part is recovered in the wash water from the scrubbers and the distillation, and the small remainder is decomposed by the small proportion of bleathing powder, the total amount recovered being practically not far from the total excess.

To this recovered acetone, carefully assayed, new acetone is added to make up the 280 pounds for the next charge.

The patentees were invited to see this apparatus and process in order to convince them that there is a strong desire to avoid any color of infringement by taking the Siemerling proportions which are excluded from their patent. But they took the ground that this was a mere evasion, or getting round their patent by using the excess of acetone over again, and could not be made to see that this, if objectionable, is so by defect in the equity of the patent, and is a proceeding that ante-dated the patent by many years. And finally they covered everything by claiming that the patent secured to them the sole right to make chloroform from acetone in the United States, thus claiming a reaction that had been well known for more than fifty years.

As to the reasons why large manufacturers of chloroform did not avail themselves earlier of the acetone process, the first answer is that it is probable that many of them, in Germany, at least, did so secretly as soon as acetone became cheaper than alcohol.

But, as to other more positive reasons, the writer, as having been for many years a large manufacturer from alcohol and as having, with all other makers, given up the manufacture rather than contest this patent, can only speak for himself. He for many years doubted the identity of alcohol and acetone-chloroform, and doubted whether the latter was as easily purified for use as the former, so that when chloroform was offered to him at so low a price as to insure that it was made from acetone it was refused. Chloroform has always been a most important agent, and during the earlier part of its career the numer-

ous fatalities from its use were charged to its impurities, so that the alcohol process was adhered to until the identity of the products from alcohol and acetone was fully proved,—not only chemically, but also by surgical experience of considerable duration. Then as time passed and the subject came up for research and reconsideration, the Siemerling results came up also and settled the question against acetone.

Finally Dr. Gustav Rumpf, a German, and an employé for some years in an acetone-chloroform manufactory in Germany, where there is no patent, came to this country, took out these patents and assigned them to the present holders, so that now for the past seven years or more any one making acetone-chloroform in this country by processes that had been free and largely used in Germany for many years, was liable to prosecution for infringement.

Having any general knowledge of the history of acetone and acetone-chloroform, it is difficult to understand how such patents could be issued that would claim to control the proportions of well known chemical materials in long known chemical reactions. But such patents were issued, and, therefore, command respect. That the processes were not used earlier in this country may be charged chiefly to the endorsements of the Siemerling paper; and that the patents appear to have been so long acquiesced in is due to the circumstance that any one who might contest them would do so at great cost of money, time and annoyance in defensive litigation, whice, if successful, would secure the benefits equally to many manufacturers, and to the public in lower prices of the products, whilst the contestant would bear all the costs.

In seeking new outlets for acetic acid the writer determined to convert the acid into chloroform, and determined also to respect these patents. In the intermediate step of making acetone, acetic acid was used, not to evade the patents, but because by its use the impurities of the crude acetates of lime were avoided, and a larger yield of better acetone was obtained. In the use of acetic acid instead of the acetates of the patent an entirely different apparatus and management are required and used, and if the patent did not exist the writer would not use either its appa-

ratus or management, but would prefer the rotary still and the continuous process.

With regard to the other step wherein the acetone is converted into chloroform, this is accomplished by a reaction that was long and well known before the date of the patent, and the proper portions of the material required for the reaction were easily obtainable by calculation, and this knowledge also ante-dated the patent. The patent then simply covers a specially devised and described apparatus and management which the writer does not use and does not want to use even if they were not patented, but much prefers his old form of apparatus and management described in 1857, and used for many years in making alcohol chloroform. And the successful use of this apparatus and management for acetone chloroform is simply in accordance with the statement of Liebig, in 1832, that acetone could be successfully used under the same conditions as alcohol.

PYRIDINE ALKYL HYDROXIDES.[1]

By A. B. Prescott and S. H. Baer.

Received January 27, 1896.

THE HYDROXIDES OF QUATERNARY NITROGEN BASES IN GENERAL.

Tetramethyl and tetraethyl ammonium hydroxides were well described by their discoverer, A. W. Hofmann,[2] in 1851. Their crystallization in a vacuum, their behavior as alkalies in reaction with the metallic salts, and their conversion to carbonates upon exposure to the air were then set forth. Various quaternary bases of mixed formation from methyl, ethyl, amyl and phenyl were made by Hofmann at the same time. The tetrapropyl ammonium hydroxide was first described by Roemer, in 1873.[3]

The decomposition of quarternary ammonium hydroxides by heat was reported upon by A. W. Hoffman, in 1881,[4] also by Lawson and Collie, in 1888.[5]

1 Read at the Cleveland meeting.

2 Phil. Trans., *1851*, (2), 357; *Ann. Chem.* (Liebig), 81, 253: 86, 292; 91, 33.

3 H. Roemer, *Ber. d. Chem. Ges.*, 6, 786.

4 *Ber. d. Chem. Ges.*, 14, 494.

5 *J. Chem. Soc.*, 53, 634.

Pyridine ethyl hydroxide was mentioned by Anderson in 1855.[1] The methyl hydroxide was reported upon by A. W. Hofman in 1881[2]. In this relation are to be considered the numerous products of the action of alkalies upon the alkyl iodides of pyridine and quinoline, obtained by Claus and by Decker, mostly in 1892 and 1893.[3]

PYRIDINE PROPYL HYDROXIDE.

Pyridine propyl iodide, prepared as stated in another paper from this laboratory,[4] was treated with moist recent silver oxide, shaking for some time in a flask, keeping down the temperature. The silver oxide for all this work was made by precipitating silver nitrate with potassium hydroxide and washing the precipitate until the washings give no color reaction with hematoxylin, to ensure the removal of the alkali. Silver oxide is sufficiently soluble in water for its solution to color litmus or phenolphthalein.

On filtering out the silver iodide, the solution of pyridine propyl hydroxide was colorless, and was found to precipitate salts of lead, silver, copper, iron, aluminum, chromium, cobalt, and nickel, an excess of the hydroxide dissolving only the precipitates of lead and of aluminum, these reactions agreeing with those of fixed alkalies. In parallel treatment with pyridine it was found not to precipitate these salts, the only apparent reaction with any of them being a blue color with the copper salt. The solution of pyridine propyl hydroxide gave the alkaline reaction with the following indicators: litmus, phenolphthalein, brazil wood, cochineal, hematoxylin, and methyl orange. Pyridine gives an alkaline reaction with all these indicators except phenolphthalein and hematoxylin, these two being capable of use in a volumetric acid estimation of the pyridine propyl hydroxide in presence of pyridine.

On heating the solution of the pyridine propyl hydroxide it acquires a red color, and the solid residue by evaporation has a black color, dissolving in water again as a red solution.

1 *Ann Chem.* (Liebig), 94, 361.
2 *Ber. d. chem. Ges.*, 14, 1498.
3 *J. prakt. Chem.* (2), 46, 106, 47, 208, 426: *Ber. d. chem. Ges.*, 25, 3326.
4 A. B. Prescott, this Journal, 18, 92.

PYRIDINE ISOPROPYL HYDROXIDE.

This base was prepared in the same manner as the normal propyl hydroxide, and it was found to give the same reactions with indicators and with metallic salts, as well as the same color when evaporated.

The isopropyl[1] base has been elsewhere stated by one of us to form a more stable iodide, of higher melting point and lower solubilities, than the iodide of the normal propyl base, and the isopropyl hydroxide has been taken, instead of the normal propyl-hydroxide, in our further experimentation.

The production of the pyridine isoyropyl hydroxide, in solution, can be made quantitatively complete as a base saturating sulphuric acid. Weighed portions of the iodine were converted to hydroxide in solution, with due precautions against loss, and the liquid titrated with tenth normal solution of sulphuric acid, using hematoxylin and cochineal, respectively, as indicators, and titrating back to the end reaction with tenth normal solution of potassium hydroxide. The hematoxylin was used in a titration to avoid interference by free pyridine, should this be present as a product of decomposition, as it does not color this indicator. The cochineal was used because it is an indicator of special delicacy for titration of pyridine alkyl hydroxides.

The results were as follows: the percentage of hydroxide *calculated* from the iodide being 55.82, the percentage of hydroxide *found* by titration with cochineal was 55.25 and 55.88, with hematoxylin it was 55.6 and 55.7

The solution of pyridine isopropyl hydroxide, on evaporation to dryness, yields a black residue, which is permanent, so that after standing three months it gives with metallic salts all the reactions of the hydroxide. The color in solution changes to red, like that of the normal propyl hydroxide. By exposure to the air it is steadily converted to the carbonate.

When the solution was treated for some time with carbon dioxide gas, then evaporated to dryness, the residue was found to bear the composition of a normal carbonate of the enivalent base. This composition was determined from the amount

1 Pyridine Alkyl Iodides, this Journal, 18, 93.

of carbon dioxide recovered in an absorption train, in ratio to the weight of iodide taken for conversion to hydroxide. The calculated weight of carbon dioxide being 14.44 per cent. of $(C_5H_5N.C_3H_7)_2CO_3$, there were obtained 14.99, 14.88, and 14.79 per cent. of carbon dioxide. In other trials the carbonation was incomplete, reaching only to 9.3, 9.47, and 10.1 per cent.

In no case was the full quantity of pyridine isopropyl hydroxide obtained in weight of the dry residue, although the evaporation was conducted under different conditions, in vacuum, in a stream of dry air, and in a stream of dry hydrogen. In the case of the carbonate, the weight of the residue did not fall below the theoretical quantity. As hydroxide the weight of the residue always fell a good deal short of the full quantity.

Pyridine isopropyl platinum chloride, perfect in proportions, was prepared from the black residue left on evaporation of the water solution of pyridine isopropyl hydroxide, by treatment in the usual manner. The black mass was dissolved in alcohol, treated with hydrochloric acid and platinum tetrachloride, and the crystalline precipitate fitted for analysis. Fine crystals were obtained, not melting below temperatures which cause decomposition.

	Calculated for $(C_5H_5N.C_3H_7Cl)_2PtCl_4$.	Found. I.	II.	III.
Platinum	29.95	30.08	30.48	30.29
Chlorine	32.58	32.50	....	32.39
Ratio of Cl to Pt	100:108	100:108	....	100:107

Pyridine isopropyl sulphate, the normal salt, was also prepared in fine crystals, by adding sulphuric acid to the hydroxide.

In various efforts to obtain the pure hydroxide in the solid state, crystalline or amorphous, vacuum desiccation, freezing temperature, formation in absolute alcohol solution, and other agencies were successively tried, without success. Crystals were not obtained, and the residue was always dark colored. Evaporation in a stream of dry hydrogen yielded a residue of the same weight as that obtained by evaporation in a stream of dry air.

These results, so far, may be summarized as follows:

Pyridine isopropyl hydroxide remains in aqueous solution for

a time without decomposition or loss in any way. The residue by evaporation of this solution, in air, or hydrogen, or vacuum, contains a considerable portion of the unchanged hydroxide, along with certain decomposition products not yet determined. The normal carbonate of this base, its normal sulphate, and its platinum chloride are easily prepared and preserved.

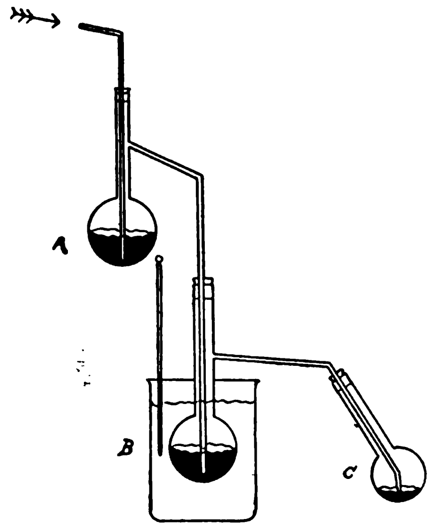
UNIVERSITY OF MICHIGAN.

ON THE REDUCTION OF SULPHURIC ACID BY COPPER, AS A FUNCTION OF THE TEMPERATURE.

BY LAUNCELOT ANDREWS.
Received January 9, 1896.

THE object of the experiments described in this paper was to determine whether there duction of sulphuric to sulphurous acid by copper take place at a higher or a lower temperature than the incipient dissociation of the former compound into water and the acid anhydride.

The sulphuric acid employed was the ordinary pure product, containing 98.4 per cent. of sulphuric acid. The apparatus illustrated in the adjoining figure was used.



The method resorted to was to heat the copper with the sulphuric acid (in flask *B*) gradually in a sulphuric acid bath, while passiug a dry current of air of carbon dioxide through it. The escaping gas was then tested (in flask *C*) by suitable reagents, to be described, for sulphuric and sulphurous acids respectively. Flask A contained concentrated sulphuric acid at the ordinary temperature (25° C.) to dry the gas, which was passed at the rate of about eighty bubbles per minute, except when otherwise men-

[1] Read before the Iowa Academy of Sciences, January 2, 1896.

tioned. The importance of securing absence of dust being recognized, the whole interior of the apparatus was washed with boiling concentrated sulphuric acid, then with water and dried in dustless air.

Experiment I.—Flasks *A* and *B* were charged with concentrated sulphuric acid and *C* with a solution of barium chloride. Air was drawn through the whole in a slow current for fifteen minutes. The solution *C* remained clear. *B* was now very slowly heated, while the current of air was maintained. Before the bath reached 70° C. there appeared in *C* a faint turbidity of barium sulphate which, at the temperature named, became distinct, but at 60° C. the solution remained unchanged even after passing the air for a long time. Hence, sulphuric acid of the given concentration begins to give up sulphur trioxide, that is, it begins to dissociate at a temperature lying between 60° and 70° C. and nearer to the latter.

Experiment II.—The apparatus was charged as before, with the addition of pure bright copper wire in *B* and with highly dilute iodide of starch in *C* instead of barium chloride. After passing air for several hours at the ordinary temperature, much of the copper had gone into solution and anhydrous copper sulphate had crystallized out, but the iodide of starch, made originally very pale blue, retained its color.

This shows that in the presence of air sulphuric acid is attacked by copper at ordinary temperature, but without reduction of the acid. The reaction must take place in accordance with the equation,

$$2Cu + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O.$$

Experiment III.—This was like the last, except that the apparatus was filled with carbon dioxide[1] and a current of this gas was substituted for air. The copper was not attacked and the starch iodide was not decolorized. The temperature of *B* was now slowly raised, and when it reached 90° C. the solution in *C* was bleached.

In a similar experiment a solution of dilute sulphuric acid colored pale straw yellow with potassium bichromate was used as an indicator for sulphurous acid in *C*. In this case the change

[1] Freed from oxygen by bubbling through chromous acetate.

of color did not occur until the temperature had risen to 108° C., the indicator being, as might be expected, less sensitive than the other.

Experiment IV.—This resembled III, except that a reagent for both sulphuric and sulphurous acid was used in *C*. This reagent was prepared by slightly acidifying a semi-normal solution of barium chloride with hydrochloric acid and then adding enough potassium permanganate to render the solution pale rose color. This indicator is capable of showing the presence of considerably less than 0.01 milligram of sulphurous acid.

When the temperature of the bath had reached 70°C. the solution in *C* was distinctly turbid with barium sulphate, but its color was unaltered. At 86° it began rather suddenly to bleach, and at 87° it was colorless. Special care was taken in filling *B* not to get any sulphuric acid on the neck or sides of the flask. A repetition of this experiment gave identical results, the gas being passed at the rate of two or three bubbles per second.

The conclusions to be drawn from this investigation are:

First. That the dissociation[1] of sulphuric acid of 98.4 per cent. begins to be appreciable at a temperature somewhat below 70°, which may be estimated at 67° C.

Second. The reduction of sulphuric acid by copper does not begin below 86°, that is, not until the acid contains free anhydride.

The assertion made by Baskerville[2] that sulphuric acid is reduced by copper at 0° is, therefore, incorrect. He appears to have based the statement, not on any demonstration of the formation of sulphurous acid, but solely on the formation of copper sulphate, which occurs as I have shown[3] in consequence of the presence of air. I believe that a repetition of his experiments under conditions securing entire absence of oxygen can but lead him to a conclusion different from that to which he now adheres.

1 The appearance of barium sulphate in *C* can not be accounted for by an assumed volatility of sulphuric acid as such, but only by its dissociation, because volatilized sulphuric acid would condense in the cold tube between *B* and *C*, since it has been shown that the acid was not appreciably volatile at the temperature of the latter. Hence only the anhydride could pass this cold tube and appear as sulphuric acid in *C*.

2 This Journal, 17, 908.

3 Traube has shown the same thing for dilute sulphuric acid. *Ber. d. chem. Ges.*, 18, 1888.

The fact adduced by him that, under certain conditions, cuprous sulphide may be formed by the action of the metal upon sulphuric acid does not allow any conclusions to be drawn respecting the presence of "nascent" hydrogen, since it may be explained perfectly well, either by the direct reducing action of the copper or by Traube's theory, which is backed up by *almost* convincing evidence.[1]

Stannous chloride will reduce sulphuric acid with formation of hydrogen sulphide, sulphurous acid and free sulphur: an analogous reaction in which the assumption of "nascent" hydrogen is inadmissible.

I hope to complete before long another series of experiments, now under way, which will form in a future communction a further contribution to the subject of the present paper.

THE OXIDATION OF SILVER.

By Charles E. Wait.

Received January 17, 1896.

IN a former paper[2] I had occasion to call attention to the large amount of silver present in a sample of bismuth litharge from a western smelting and refining company. The silver in this instance estimated in the metallic state was 2.94 per cent.

There was some doubt expressed as to the condition in which the silver existed, it being usually reported in the metallic state. Upon investigation it was found, as was shown in the paper referred to, that the silver did not exist wholly in the metallic state, but partly in another form, probably the oxide.

The conclusions reached at that time were based upon the fo lowing experiments:

1. A weighed sample of the litharge was boiled in acetic a for about half an hour, the solution was filtered, and the fil trate gave no reaction for silver.

2. Same as above, but with continued boiling, the fil gave no reaction for silver.

3. A sample was placed in cold acetic acid, kept the hour, then heated to boiling, the solution was fi itated, and in the filtrate silver was fo per cent. of the silver in ly agreeing res

it is interesting to note that the residue contained grains of metallic lead, or argentiferous lead.

I have placed the following interpretations upon the above results:

In Nos. 1 and 2 if any silver in any form was dissolved in the acetic acid, it was in turn reprecipitated by boiling, in the presence of metallic lead.

In No. 3 the silver dissolved, did not in all probability exist in the metallic state; and in this case was not precipitated by the lead, or argentiferous lead, the solution being brought merely to the boiling temperatnre.

I have been led to the above interpretations by showing that neither metallic silver reduced to fine subdivision by mechanical means, nor silver freshly prepared by zinc from silver chloride is soluble in acetic acid, while argentic oxide is soluble in that acid; and a solution of silver oxide in acetic acid was precipitated completely by metallic lead upon boiling.

If the oxides are decomposed at a temperature of 300° C.,[1] or less,[2] how may we account for the existence of this substance in a product so highly heated as the litharge from the refining furnace?

Berthier[3] has observed that lead may be oxidized by oxide of copper, when melted together, and further consideration of the subject shows that certain metals may be oxidized by being melted with an oxide of another metal, this oxidation depending in all probability upon the excess of the oxide present. Silver does not appear to be oxidized by oxide of copper if the results in experiment No. 18 are trustworthy.

According to Fournet's experiments[4] silver is not an exception to the metals to which litharge gives up a part of its oxygen when fused with them for a considerable time.

While it is true that in the process of cupellation there is a loss of silver due possibly to oxidation, yet I do not find any losses even in the most exaggerated cases at all comparable with the percentage of silver oxide which I have been able to produce by a simple, yet possibly new, method.

It seemed to me an interesting problem to astertain, if possible, the condition under which silver may be oxidized at a high

1 Roscoe and Schorlemmer, Vol. II, Part I.
2 *J. Chem. Soc.*, 65. 316.
3 Crookes and Rohrig, Metallurgy.
4 Erdman's Journal.

temperature, and the conditions under which the oxide of silver, if thus formed, would remain as such.

Some interesting work has been done along a similar line,[1] that is, a study of those oxides which are stable at high temperature, and those which are decomposed, but under neither head does silver seem to have been discussed.

So few observations have been made along this exact line, as far as I have seen, that I have been induced to make some investigations with a view to throw light upon the subject, if possible.

The general method of conducting the experiments, I will briefly state as follows: Metallic silver in minute subdivision was incorporated with one of the several bodies mentioned below; this mixture was put in a cupel of bone ash, or in a scorifier, and then placed in a muffle of an assay furnace and subjected to an oxidizing heat.

After this operation the mass was removed to a mortar, pulverized, then digested with acetic acid to boiling, the solution was filtered ; in case a lead compound had been used, the lead was removed by sulphuric acid, and hydrochloric acid was then added. The silver chloride thus formed was filtered, dried, and wrapped in least pure lead foil and then carefully compelled.

There was thus obtained the silver, which was converted to argentic oxide,—at least I assume it to be such,—and it is interesting to note that the amount of silver converted to oxide, and tabulated below, shows a very great range, in fact from only a trace to as much as thirty-nine per cent. of the silver used.

This variation seems dependent upon a number of conditions, namely: the body with which the silver was mixed, duration and condition of heat, whether low, medium, or high temperature. As I did not use a pyrometer to ascertain the temperature during these experiments, I have thought it desirable to indicate the degree of heat approximately by such terms as "low," "medium," and "high," referring to the condition of the heat as usually obtained in the muffle in the assay of silver.

I append herewith several tables of experiments and results:

[1] *J. Chem Soc.*, April, *1894*.

TABLE A.

No. experiment.	Ag in gram.	Heated with	Time of heat	Condition. of heat.	Per cent. Ag as Ag_2O.
1	0.5	2.5 grams MnO_2.	60 min.	medium	9.40
2	0.5	5.0 " MnO_2.	60 "	"	7.78
3	0.5	2.5 " Fe_2O_3.	60 "	"	none.
4	0.5	2.5 " Bi_2O_3.	60 "	"	"
5	0.5	2.5 " ZnO.	60 "	"	"
6	0.5	2.5 " $CaCO_3$.	60 "	"	"

From the above it will be seen that silver oxide was produced, and remained as such where manganese dioxide was used and in no other case; it would also seem that this oxide was made at the expense of the manganese dioxide and not by atmospheric oxidation, nor does it seem to have been produced in experiment 3, (certainly not remaining as such) assuming the possible conversion of Fe_2O_3 to Fe_3O_4.[1]

TABLE B.

No. experiment.	Ag in gram.	Heated with	Time of heat.	Condition. of heat.	Per cent. Ag as Ag_2O.
7	0.5	7.5 grams MnO_2.	30 min.	medium.	34.16
8	0.5	10.0 " MnO_2.	30 "	"	18.84
9	0.5	3.0 " $CaCO_3$.	60 "	"	none.
10	0.5	3.0 " Fe.	60 "	"	"

The above results show that silver oxide was produced in the presence of manganese dioxide only; that less duration of heat than in Table A gives the amazing large per cent. of that oxide, and it furthermore seems that the oxide produced is not in proportion to the manganese dioxide used, but the reverse condition is generally seen in each set of experiments.

TABLE C.

No. experiment.	Ag in gram.	Heated with	Time of heat.	Condition of heat.	Per cent. Ag as Ag_2O.
11	0.5	1 gram MnO_2.	2.5 min.	high.	32.24
12	0.5	2 grams MnO_2.	2.5 "	"	34.28
13	0.5	2 " MnO_2.	20 "	"	11.72

The above experiments show, other conditions being the same, the longer the duration of the heat the less oxide there is produced.

[1] *J. Chem. Soc.*, 65, 313.

TABLE D.

No. experiment	Ag. in gram.	Heated with	Time of heat.	Condition of heat.	Per cent. Ag as Ag_2O.
14	0.5	5 grams PbO.	10 min.	medium.	38.85
15	0.5	4 " PbO_2.	10 "	"	35.11
16	0.5	2 " BaO_2.	5 "	"	12.28
17	0.5	7 " BaO_2.	10 "	high.	2.04
18	0.5	4 " CuO.	12 "	"	none.

In Nos. 14 and 15 the mixtures were placed in scorifiers, and covered with ten grams of lead oxide.

In Nos. 16 and 17 the mixtures were placed in cupels and covered with two grams of barium dioxide.

It is interesting here to notice that barium dioxide serves as an oxidizing agent; that the amount of silver oxide produced decreases probably both with increase of time and temperature.

Although lead dioxide may readily give up a part of its oxygen and thereby be converted into a lower oxide, yet the amount of silver oxide produced was no greater than with lead oxide alone; this is an interesting illustration of the property of lead oxide to serve as a possible carrier of atmospheric oxygen, producing silver oxide in a manner similar to that of the two bodies, manganese dioxide and barium dioxide, liberating oxygen. In the case of lead oxide, No. 14, if dissociation is not possible[1] even at so high a temperature as 1750° C., it seems most reasonable to account for its peculiar oxidizing action, as mentioned above; *viz.*, as a carrier of atmospheric oxygen. Although copper oxide has been shown to yield up a part of its oxygen at 1500° C., yet I find no evidence of silver oxide existing in experiment 18 in the remaining ignited mass.

TABLE E.

No. experiment.	Ag_2O in gram.	Heated with	Time of heat.	Condition of heat.	Per cent. Ag as Ag_2O.
19	0.5 Ag_2O.	5 grams MnO_2.	60 min.	medium.	36.4
20	0.5 Ag_2O.	3 " Fe.	60 "	"	0.3
21	0.5 Ag_2O.	3 " $CaCO_3$.	30 "	"	0.2

In Table E a variation was made in the nature of the experiment. Freshly prepared silver oxide was used; while this oxide was completely decomposed upon being heated gently upon a porcelain lid, yet in No. 19 where manganese dioxide

[1] *J. Chem. Soc.*, 65, 316.

was used, it will be seen that 36.4 per cent. of this silver oxide completely escaped decomposition.

The above results, in connection with others along a similar line, have induced me to believe that attention has not heretofore been directed to the ease with which silver may be oxidized by lead oxide, and particularly by substances which give up a part of their oxygen upon gentle ignition, such as manganese dioxide and barium dioxide. It is not then reasonable to assume that certain losses, or irregularities in the treatment of silver and its compounds, may be due to this cause?

UNIVERSITY OF TENNESSEE.

THE DETERMINATION OF THE SOLID FAT IN ARTIFICIAL MIXTURES OF VEGETABLE AND ANIMAL FATS AND OILS.

BY J. H. WAINWRIGHT.
Received February 1, 1896.

IT will be readily conceded by most analysts that there is no subject in analytical chemistry presenting more difficulties than the examination and analysis of the fixed oils and fats. This is especially true in the case of mixtures of oils of different origin, and there is probably no problem more difficult to solve in most cases than the analysis of such a mixture when even approximately correct quantitative results are required.

It is only within a comparatively recent period that the investigations of the chemist have been especially directed to this branch of research as formerly the character and identity of a sample of unknown origin was chiefly, but very doubtfully established by means of obscure color reactions and one or two simple determinations, such as specific gravity, melting point, etc.

At present, however, the investigations of many learned chemists have shown that determinations of the chemical and physical properties of a sample, such for example as the combining weight of fatty acids, the percentage of iodine the sample will absorb, the percentage of volatile fatty acids, etc., will yield results by which may be established, in most cases with reasonable accuracy, the fact as to whether it is a simple oil or fat, such as olive, linseed, lard, butter, etc., and if so its iden-

tity and quality; or, if adulterated, to determine with a fair degree of accuracy the character and probably extent of adulteration. This is especially the case when a mixture consists of but two oils or fats, one of which is known, in which case a few quantitative determinations will usually enable the analyst to readily astertain its approximate composition.

If a sample, however, consists of a mixture of *more* than two oils or fats, any statement of its composition calculated from the results of such determinations as above mentioned would be of extremely doubtful accuracy in any case, even if one of the constituents were known, and even then it would be at best but a broad approximation owing to the variations in chemical and physical properties exhibited in different specimens of the same kind of oil.

Some years ago samples of compound lard for export were submitted to the United States Laboratory for analysis with a view to determining the relative proportions of its constituents in order that the claim of the exporter for "drawback" of duties paid on one of its constituents might be verified.

This "compound lard" or "lard compound" has in recent years become an important article of commerce and consists essentially of cotton-seed oil and oleostearin made from beef fat mixed in different proportions; and sometimes containing a small percentage of genuine lard. Its composition is variable according to the brand and particular formula by which compounded, but is generally about as follows:

	Per cent.
Oleostearin	20 to 30
Cottonseed oil	70 to 80

or

Oleostearin	18 to 30
Lard	10 to 20
Cottonseed oil	65 to 75

In the first case determinations of the properties of the sample would disclose its composition with reasonable accuracy, but in the second case considerable time was spent, I might almost say wasted, in making a long series of these determinations, both on the samples themselves and on mixtures made in the labora-

tory in accordance with the formula for comparison, without arriving at any satisfactory conclusions, until finally a very simple method for the analysis or rather assay of these "lard compounds" was devised, which up to the present time seems to yield fairly satisfactory results.

About 150 grams of the sample is placed in a beaker and heated in a boiling water-bath untilentirely melted. The water is kept boiling for at least one hour and is then allowed to cool gradually without removing the beaker from the bath until the temperature is reduced to about 75°–80° F. It is then allowed to stand for at least twelve hours in a moderately warm place.

In practice the beaker immersed in the warm water of the bath is left standing in the laboratory over night at the ordinary room temperature which is usually all that is necessary excepting in very warm weather when the temperature should be reduced by artificial cooling.

This process causes the solid fat to crystallize, which being accomplished, fifty grams of the sample is weighed from the beaker after its contents have been thoroughly mixed by means of a glass rod or spatula, and is carefully wrapped in a double thickness of Canton flannel in which it is subjected to pressure in a small screw press.

The pressure should be applied very gradually, especially at first, and should be continued until the screw has been forced down as tightly as possible. After standing a few minutes to permit the oil to drain off, the contents of the press are removed and the cake of solid fat, consisting essentially of stearin, is easily separated from the cloth in which it is wrapped and can then be weighed.

The press used is called "Osborne's Patent Beef Press," and can be obtained in almost any hardware store, and is used for domestic purposes, such as the preparation of "beef tea," etc.

The length of time required is usually at least one hour, and the temperature seems to be a matter of comparative indifference provided, of course, extremes are avoided.

No great accuracy is claimed for this method, and that it is based on any thing like *strictly* scientific principles remains to

be proved, but the following results will, I think, show that it is what it is claimed to be, *i. e.*, a useful, if rough method for the assay of these manufactured compounds, and it is especially valuable as a preliminary operation in the more extended process of analysis.

Mixtures of the various ingredients, *i. e.*, oleostearin, lard and refined cottonseed oil were made in the laboratory, of which the following, as well as many others, are typical examples :

No. 1.

	Grams.
Oleostearin	20
Lard	10
Cottonseed oil	70

No. 2.

Oleostearin	25
Lard	10
Cottonseed oil	65

No. 3.

Oleostearin	25
Cottonseed oil	75

No. 4.

Oleostearin	24
Lard	10
Cottonseed oil	66

which, when assayed by the above described method, yield respectively :

Number.	Per cent.
1	19.6
2	25.2
3	25.8
4	25.2

The following are the results obtained with samples of different formulas submitted for analysis :

SAMPLE A.

	Per cent.
Oleostearin	30
Cottonseed oil	70

SAMPLE B.

	25
	10
	65

SAMPLE C.

Oleostearin	25
Cottonseed oil	75

SAMPLE D.

Oleostearin	25
Lard	10
Cottonseed oil	75

SAMPLE E.

Oleosterian	25
Cottonseed oil	75

SAMPLE F.

Oleostearin	23
Lard	10
Cottonseed oil	67

SAMPLE G.

Oleostearin	23
Lard	10
Cottonseed oil	67

SAMPLE H.

Oleostearin	24
Lard	10
Cottonseed oil	68

SAMPLE I.

Oleostearin	25
Cottonseed oil	75

which, upon assay as above, gave the following percentages, respectively:

	Per cent.
A	29.2
B	26.4
C	24.4
D	26.2
E	25.2
F	24.6
G	23.9
H	24.4
I	24.5

All of the above assays would seem to show that the results yielded are correct to within about one and a half per cent., and in my opinion it would be perfectly safe to consider that as a reasonable margin of error.

In consideration, however, of the character of the process of

assay as well as the character of the mixture and of the samples analyzed, I do not believe the analyst would be justified in reporting any *exact* amount of oleostearin found and have therefore adopted the form of reporting that the sample submitted contained "not less than —— per cent., nor more than —— per cent.," the margin of the error being as stated.

UNITED STATES LABORATORY.

THE MEASUREMENT OF THE COLORS OF NATURAL WATERS.

BY ALLEN HAZEN.

Received January 30, 1896.

THE diffusion of more accurate information and more rational theories as to the causation of diseases during the past few years has resulted in simplifying and changing many of the problems presented in connection with the chemical analysis of public water supplies. The healthfulness of a water for such use is determined to a much greater extent than formerly, by critical inspections of the sources of supply, particularly in the case of surface waters; and information as to the size of the water shed, flow at different seasons, amount of storage and character of the storage reservoirs, together with full information in regard to the population on the water shed and the way it disposes of its sewage, are more important and frequently adequate in themselves to determine the wholesomeness or unwholesomeness of a water; and the use of chemical analysis in connection with the investigation of such problems is rather in serving as an index of the varying amounts of contamination at different times, than in showing the presence or absence of substances which are in themselves injurious to health. Bacterial examinations also, which have become so frequent and necessary in connection with analyses of this character, play also their part in measuring such fluctuations.

There are, however, several determinations which indicate in themselves substances desirable or undesirable in a public water supply, and among these perhaps the most important are the hardness, the color, and in the case of ground water supplies, the iron; and although the color is determined mainly for its own

sake, and because a colorless water is more desirable that a colored water, and not because of any direct relations that the results obtained may bear to the wholesomeness of the supply, the interest that attaches to the determination often makes it of no less importance than those of the ammonia or other organic constituents.

The importance of this question of color has long been felt, and numerous efforts have been made to devise means for measuring and recording the colors. The essential requirements of such a method are that the figures obtained for a given color shall be the same at all times and in all places, and that it shall be possible to reproduce the colors with certainty at any future time. It is also desirable that the figures obtained shall be as nearly as possible proportional to the actual apparent colors of the various waters, as seen under ordinary conditions.

Perhaps the simplest method of measuring the colors of waters consists in taking a solution with a color of substantially the same hue as the waters to be examined, and diluting it with various quantities of distilled water, producing a series of colors with which the waters may be compared and results of relative colors obtained. The most natural substance to use for the colored solution is a highly colored swamp water, but the results obtained with such a standard of color, although comparable among themselves, would hardly have further permanent value owing to uncertainty as to the color of the water used for comparison, and the certainty that this color would fade, and the impossibility of reproducing it with accuracy at a future time. It is evident that any such procedure cannot fairly be considered as establishing a standard of color, and that the colors must have some definite physical basis which can be formulated and described with certainty and which will allow them to be reproduced at pleasure.

Perhaps an ideal basis of description of color would be a statement of the changes in the numbers and intensities of the vibrations in white light produced by passing through a layer of the water under examination. These changes are, however, so hopelessly complex as to defy even the hope of ascertaining them, and even if they could be determined it is doubtful if a statement of them could be made simple enough to convey any

meaning to the ordinary mind as to the colors represented.

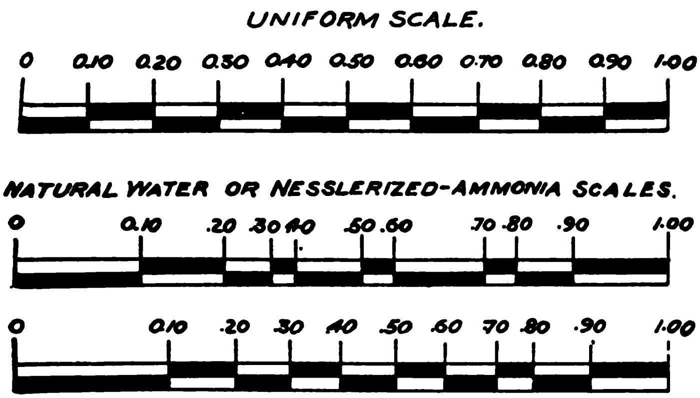
The most satisfactory standard which we can reasonably hope to realize is probably furnished by some other substance with a definite color, which can be produced at will, and which can be compared with the colors of waters, furnishing results of permanent value. One of the first attempts at such a standard was made by Messrs. Crooks, Odling, and the late Dr. Tidy,[1] who used solutions of ferric and copper salts in solution in independent vessels, which, superimposed upon each other, produced a color equivalent to that of the water. The fatal objection to this standard was that the color of the iron solution depends very largely upon the formation of basic compounds which vary in the intensity of their colors with very slight variations in acidity and with changes in temperature, so that the results obtained are open to a most objectionable uncertainty.

Another, and in some respects more satisfactory, attempt in establishing a standard was made by Prof. A. R. Leeds,[2] who suggested that extremely dilute solutions of ammonia after being nesslerized should be taken as the standards of color, the quantity of ammonia being taken as an index of the color produced. This standard was certainly most convenient, as the nesslerized ammonia standards are always present in laboratories for water analysis being required for another purpose, and it was believed that the colors had a sufficiently definite value to form a reliable standard.

This method has been widely used in the United States, and was employed by the author for several years and for the examination of some thousands of samples of water, until it became apparent that the variations and discrepancies in the results obtained were so great as to require serious consideration. As a result, a critical examination of the colors produced in this way was undertaken with the aid of my then assistant, Mr. Harry W. Clark, the results of which were published in full in the *American Chemical Journal*, **14**, 300. It was found in the course of the investigation that the colors produced depended not only upon the amount of ammonia used, but also upon a

[1] *Chem. News*, 43, 174.
[2] *Proc. Am. Chem. Soc.*, 2, 8.

whole series of conditions, many of which were not capable of exact control, so that the results obtained varied among themselves, even in the same laboratory at different times, to a most unsatisfactory extent. It was found that the colors produced depended not only upon the composition of the Nessler reagent and the quantity used, but even upon the way in which it was applied to the water containing the ammonia, and to a very



Irregularities in Nesslerized Ammonia and Natural Water Standards: From Report by Mr. FITZGERALD and Mr. FOSS in Report of BOSTON WATER BOARD for 1893.

large extent upon the temperature at which the experiment was made. It was further found that the colors produced were not at all proportional to the quantities of ammonia present, even under the most favorable conditions, owing in part to the very considerable color of the Nessler reagent itself, and in part to the fact that small amounts of ammonia produce less color relatively than larger quantities; and as a result of the combination of these two causes the colors increase in an irregular way that is most unsatisfactory. This irregularity of increase is well shown by a cut here reproduced from the report of Mr. FitzGer-

ald and Mr. Foss in the report of the Boston Water Board for 1893,[1] showing the colors of nesslerized ammonia and natural water standards received from the Institute of Technology when read against a single natural water standard in an ingenious colorimeter devised by the authors, and in addition the difference between the two lower scales shows how the standard differed at two different times.

The nesslerized ammonia standard has been improved in an important way by Mrs. Ellen H. Richards, of the Massachusetts Institute of Technology, who has for some years used standards of natural waters diluted with distilled water, as suggested above, and diluted to such an extent as to correspond with the nesslerized ammonia standards at a number of selected points, and with intermediate and lower standards prepared by interpolation between the selected points of comparison. This method of procedure eliminates to a certain extent the daily fluctuations in the values of the nesslerized ammonia standards, and also tends to smooth out the smaller irregularities in the scale, although the larger ones could hardly be removed without destroying the integrity of the scale itself. The method of procedure is, moreover, open to the more serious objections to the nesslerized ammonia standard in that the standards themselves depend for their original values upon the nesslerized ammonia standards of which the exact values are always open to question.

In a recent article published in the present volume of this Journal, page 68, by Ellen H. Richards and J. W. Ellms, an account is given of an attempt to establish in a more accurate and permanent manner the value of the standards used by comparing them with the Lovibond "Tintometer." This instrument consists essentially of a series of colored glasses which are superimposed upon each other to produce a color equivalent to that of a given sample of water or other substance. The tintometer in its construction and operation is so complicated as to render it impracticable, as Mrs. Richards states, to use it for the direct determination of colors in waters where many samples have to be examined, and its use is thus limited to determining

[1] *Franklin Institute*, 138, 91.

from time to time the values of the standards actually used for measuring the colors which would otherwise be subject to uncontrolled variations.

Several objections may be raised to the use of the Lovibond Tintometer as an ultimate standard of color. If we admit that the colors of the glass slips are permanent and will forever hold their color, we still depend upon the honesty and skill of the manufacturer of the instruments to produce glass slips of precisely the same values as those used in the original apparatus. It is of course conceivable that an apparatus should be continued in use with the same slips for many years, but eventually the slips would become worn or scratched and would require to be replaced, or the apparatus might be destroyed by fire or other accident; and in any case other laboratories buying new instruments will require to have new slips. It is thus seen that the values of the colors depend ultimately upon the honesty and skill of the manufacturer in preserving and reproducing an arbitrary standard, and not upon natural units.

It may be said as against this view that the values of the Lovibond units have been determined by comparison with the colors of solutions of definite chemical composition with such care and precision that it will be possible at future times to determine whether the slips then in use are really the equivalents of those now sold, and that it would even be possible to reproduce them in case the present standards were lost or destroyed. But against this statement it may be urged that it is much more rational, simpler, and better in every way to compare the waters directly with the chemical solutions which are the ultimate points of reference without the intervention of glass slips or other standards.

An attempt to do this was made by the author, who published[1] a description of a method of comparing the colors of waters with those of solutions of platinum and cobalt of known strength, the colors of which were absolutely definite and permanent, and capable of being reproduced with precision at any time, and not affected by temperature or other conditions likely to occur in well regulated laboratories. The method of stating the results

[1] *Am. Chem. J.*, 14, 300.

was a natural and simple one, namely, "that the color of a water is the amount of platinum, in parts per ten thousand which, in acid solution, with so much cobalt as will match the hue, produces an equal color in distilled water."

Since the publication of this article the platinum standard has been used in laboratories under my direction, and by my successors, and in other and independent laboratories for the measurement of colors in many thousands of samples of water, and with such uniformly satisfactory results[1] that I believe it only fair to say a word in regard to the objections raised to the standard by Mrs. Richards in the above mentioned article.

The first of these objections is that there is an excess of orange to yellow in the standard, which, if I understand the language correctly, means that the standard is redder than the waters to be examined. This contingency was provided for in the original article by making the platinum the standard of color and allowing the cobalt to be varied as required to match the hues of the waters. The quantity of cobalt in proportion to the platinum which I suggested, namely, one-half as much metallic cobalt as platinum, was the result of my experience of thousands of samples of water prior to the publication of that article, but as waters from different sources vary in their hues, it was fully recognized that it might be desirable in other cases to use a different proportion of cobalt from that suggested; and if it is found that the quantity of cobalt suggested produces a standard too red for a given set of waters, it is only necessary to make a fresh standard with a somewhat smaller quantity of cobalt to be determined by experiment, when it will be found that the hue matches the waters as closely as it is possible for any single standard to do.

As a matter of fact, standards containing a quarter less and others containing a quarter more cobalt than the amount suggested have been repeatedly used by the author and by others for special purposes, and, while the hues of some waters are more accurately matched, the results as a whole have hardly warranted any change in the proportion suggested for ordinary practical work.

1 Report of Boston Water Board, 1893, p. 85. Report of Massachusetts State Board of Health on Metropolitan Water Supply, 1895, p. 177. *J. Franklin Institute*, 138, 403.

The second objection is that the standard is not suitable for the measurement of the deeper colors. This is indeed an important question, and had been thoroughly canvassed by the author and his assistants before the publication of the process, and the means for avoiding difficulties from this source were distinctly stated in the article, although the reasons for the precautions to be taken were not perhaps stated as fully as was desirable.

One of the first facts to be learned by persons studying the colors of solutions is that solutions having the same color in one depth or dilution are not necessarily of the same color in greater or less depths or dilutions. The truth of this statement was most strikingly shown in an article published by the author, in connection with Mr. Harry W. Clark[1] in connection with the colors of the various nitrophenols in various dilutions, in which it was shown, for example, that alkaline solutions of ortho- and paranitrophenols are of about the same color when solutions containing one-tenth or a part in a million of nitrogen are seen in depths of 200 mm., while with more dilute solutions the para is more highly colored, and with more concentrated solutions the ortho has the deeper color, and the variations are so astonishingly great that with the most concentrated solutions examined the ortho produced as much color as more than thirty times its weight of paranitrophenol.

The explanation of this remarkable phenomonon has been clearly given by Mr. Desmond FitzGerald and Mr. William E. Foss, in the annual report of the Boston Water Department for 1893.[2] It is there stated that the amount of light which passes through successive equal layers of an absorbing solution diminishes in geometrical progression as the number of layers increases in arithmetical progression; and as the coefficient of transmission varies with different solutions, it often happens that a water matches the standard very closely in hue in a short depth, but appears of quite a different hue in a greater depth. That is to say, taking an extreme case, the coloring-matter in one solution, owing to its chemical or physical properties, absorbs a large percentage of the light from a narrow band of the spectrum,

[1] *J. Anal. Appl. Chem.*, 5, 301.
[2] *J. Franklin Institute*, 138, 401.

while another substance to produce the same apparent color absorbs a small percentage of the light from a broad band in the spectrum. In the first case as the solution is increased in depth or concentration, its color at first rapidly increases until all or nearly all of the rays of light which it is capable of absorbing are exhausted, and further increase in depth effects but little further change in color. In the second case, owing to the smaller percentage absorption of the light rays the color increases to a much higher limit, and in great depths the solution has a much deeper color than is possible in the former case where the action is confined to a narrow band in the spectrum.

A combination of absorption bands having different relative absorptions in the same solution gives rise to the change in hue so often noticed with changing depth or dilution. Thus it is a matter of common experience that a water which is a pure yellow or even greenish when seen in slight depth becomes orange and even quite red when seen in great depths. The way in which these differences occur was well shown by a diagram, in the report mentioned, showing how the standard matching the water at low depth, constantly diverges from it as the depth increases.

There are two possible means of remedying this evil. The first would be to secure a standard in which the coloring-matter was identical in composition with the coloring-matter in the natural waters. Such a standard could obviously be only the natural water standard which, as shown above, is really no standard, but only a go-between between the waters and the real standards. The other method of avoiding the difficulty is to make comparisons only in such deqths that the divergencies between the standards and the waters will not be considerable.

As stated in the report quoted above, the quantity of light transmitted decreases in geometrical progression as the depth increases in arithmetical progression. Let us say that the first cm. of water intercepts one per cent. of those rays of light, whose interception produces the effect of color in the water. The second cm. of water will then intercept one per cent. of the remaining rays, or 0.99 per cent., and the third cm. will intercept one per cent. of the 98.01 per cent. reaching it, or substan-

tially 0.98 per cent., leaving 97.03 per cent. As the color produced is measured by the difference between the light remaining and the full light, we may express the colors produced by one, two, and three cm. of water as, respectively, 1, 1.99, and 2.97. These figures are obviously substantially proportional to the depths; the error of one per cent. in the last case being entirely too small to be taken into consideration. If, however, the process is carried further, the error increases as rapidly as the square of the depth, and at no very remote point becomes important and serious. As an illustration of the substantial correctness of this proposition, the above-mentioned ortho- and paranitrophenols may be mentioned. Notwithstanding the most extraordinary differences between the colors of the comparatively concentrated solutions of these substances, the colors produced by extremely dilute solutions are substantially proportional to the amounts of the respective substances present, and so long as certain limits are not passed, their colors increase at the same rate with increasing depth. The differences between these substances at various dilutions are, however, vastly greater than those between the platinum-cobalt standard and natural waters, and the differences in the latter case with increasing amounts of color are no greater than would be sure to be found with almost any two coloring-matters not of the same chemical composition.

The point to which it is safe to carry the reading of colors is determined by practical experiment and not by theoretical considerations. It was stated by the author in the original paper that up to a point corresponding to colors of 0.9 in a depth of 200 mm., or corresponding lighter or deeper colors in greater or less depths, the variations between the hues of the platinum standard and actual waters were so slight as to be unimportant. In Mr. FitzGerald's report mentioned above, it is stated that colors up to a depth of 1.0 for the same depth can be satisfactorily compared with the platinum standard, this limit being ten per cent. above that suggested by the author, and as long as colors are not measured above these depths the errors introduced are entirely unimportant; and while it is recognized that serious errors might be introduced by the attempt to read much deeper colors, this contingency was distinctly provided against by stat-

ing that all waters with deeper colors should be read in a less depth of liquid, or what is practically more convenient, and as far as I have been able to ascertain, equally accurate, the water should be diluted with one, two or more times its volume of distilled water, the color of the diluted water read and multiplied by a proper factor. Mrs. Richards finds it necessary to adopt this same procedure, even with the natural water standards, because, as a matter of fact, the coloring-matters in different waters vary from each other, and the hues produced in different depths also vary in the same way as the hue of the platinum standard varies from that of a water, only in a less degree, and with the natural water standards it is only possible to read accurately colors as high as 2.0, or only twice as high as the limit with the platinum standard.

This dilution of waters with high colors may be objected to on the ground that, a water having, for example, a color of 2.0 does not in reality contain twice as much coloring-matter as a water with a color of 1.0, and that correct results will not be obtained in this way. This is, in fact, the case with the nesslerized ammonia standards and with the natural water standards based upon them, as was shown by the author, who stated that with these standards "color 0.5 is only twice as deep as color 0.2; color 0.8 is only twice as deep as color 0.3; color 1.0 is only twice as deep as color 0.4, etc.;[1] and this very fact is one of the serious objections to the use of these standards. With the platinum standards, on the other hand, the numbers expressing the colors, as nearly as can be determined, are proportional at every point to the actual coloring-matters present, and this simple relation is one of the important practical advantages of the standard.

As a matter of fact, a great majority of the waters, even from swampy regions, have colors low enough to allow accurate direct readings with the platinum standard, and the necessity of diluting the more deeply colored waters occasionally found cannot be regarded as a practical objection to the process. In actual use the convenience of operation, the simplicity of the apparatus required, the accuracy of the work obtained even with unskilled

[1] *Am. Chem. J.*, 14, 308.

operators, and the permanency of the standard, even under exceptionally unfavorable conditions, which has far exceeded anything for which we dared to hope when the standard was first used, have abundantly demonstrated its utility; and in view of the ease and accuracy with which it is possible to compare directly the colors of natural waters with metallic solutions, which are, in fact, the only reliable ultimate standards now in use or known, it seems most unfortunate and in every way undesirable to introduce arbitrary go-betweens, not having definite values of their own or capable of being reproduced or controlled except by comparison with other standards.

TECHNICAL ANALYSIS OF ASPHALTUM. No. 2.[1]

BY LAURA A. LINTON.

Received January 3, 1896.

MY former article[2] on this subject has been so favorably received and commented upon that I have been encouraged to offer a second contribution with the object of adding a few more facts to the literature of the subject, as well as to point out certain changes in the method of analysis outlined in the first article, which changes have been suggested by recent analytical work.

The method universally employed for the determination of the incorporated water of asphaltum is that of estimating the loss in weight of the substance when exposed to a temperature of 100° C. The possibility of a loss of more or less of the inherent volatile matter when heated to such a high temperature must have occurred to every one engaged in the analysis of asphaltum. A series of experiments made during the past few months has confirmed my suspicion that such is the case.

The experiment proper consisted in heating a weighed portion of asphaltum in a combustion tube, the general arrangement of the apparatus being the same as that employed in the determination of water in organic analysis. The temperature was gradually raised from the temperature of the room to that of boiling water. The tube was swept out before and after heating with either dried air or dried hydrogen. Simultaneously with

[1] Read at the Cleveland meeting, December 31, 1895.

[2] This Journal, 16, 809.

this experiment two other weighed portions of the same asphaltum were dried, one in an oven at 100° C. to serve as a check upon that portion dried in the combustion tube, while the other portion was dried in the sun.

As the method of sun drying requires several days it was done in a room as free as possible from dust and, to increase the temperature and at the same time to exclude all foreign matter, the samples were placed in large watch glasses with watch-glass covers fitting loosely to allow of circulation of air. In this lens-like arrangement the maximum temperature did not exceed 50° C. On cloudy days the drying was necessarily done in the oven below 50° C.

These experiments showed that the asphaltum tested did not oxidize below 100° C., as aspiration with dried air and dried hydrogen gave the same results; and also that all moisture is driven off below 50° C. while between 50° C. and 100° C., a certain portion of oily matter is lost, this oil invariably collecting in drops about the mouth of the combustion tube. In the light of these facts it becomes clear that the old method of determining moisture, if it is to be determined at all, is incorrect since the percentage lost on heating the asphaltum to 100° C. includes not only the water but also that part of the petrolene volatile below 100° C.

The moisture associated with an asphaltum being hygroscopic, as in evident from the fact that the same specimen carries a constantly varying proportion depending on atmospheric conditions, it should never be estimated as a constituent part of the asphaltum, particularly in making analyses for purposes of comparison.

In making all of my recent analyses, as a preliminary, I have air dried to a constant weight several grams of the sample to be analyzed before weighing out the portion to be treated with the different solvents, thus entirely excluding water from the percentage composition of the asphaltum.

A second departure from the method previously given is a purely mechanical one. As a matter of convenience I have discarded the use of the Erlenmeyer flask, the substance being weighed out on balanced filter-papers instead. In this way all digestion is done in separatory funnel. This method of treat-

ment is very simple and the results obtained are good, but care must be taken that the solution in the funnels does not become too concentrated before running off through the tap, otherwise the petrolene precipitates itself, more or less of it adhering to the outside of the filter-paper. To prevent this the petroleum either may be drawn off every few minutes until the greater part of the petrolene has been extracted after which it is perfectly safe to allow the digestion to continue for hours in removing the final traces.

Lastly, I have obtained some interesting and, in my opinion, important results by fractionating the asphaltene, determining it in two portions; that soluble in boiling turpentine and that soluble only in chloroform. The process is a very tedious one on account of the difficulty of removing the very last trace soluble in boiling turpentine, but the results that follow are a sufficient warrant for the expenditure of so much time, which, for the specimens analyzed, ranged from one to four weeks. In order to secure concordant results in duplicate analyses I found it necessary to pursue the following course:

After the removal of the petrolene the residue on the filter was digested in boiling turpentine until the filtrate was colorless, when the contents of the filter were washed in alcohol and dried at 100° C. If, on drying, a black, semi-liquid substance separated from the mass, this was an indication that the turpentine fraction had not been entirely removed, in which case the process was repeated. In the most refractory specimens this treatment was applied many times. The tardy yielding to the solvent power of the turpentine is doubtless largely due to the fact that the turpentine does not readily penetrate the mass and it may be, also, that the chloroform fraction prevents the action of the turpentine just as gold protects silver from the action of nitric acid. The completion of the process is always indicated by the appearance of the dried residue which, after the complete removal of the turpentine fraction, is invariable a loose, brown powder without coherence. This treatment shows that part of the asphaltene soluble in boiling turpentine to be a black, viscous, semi-liquid substance resembling tar and having a melting point at or below 100° C.

Another fact, which may prove valuable as well as interesting, is clearly brought out in this fractionation of asphaltene and that is that not only do the "aged" varieties of asphaltum contain a larger petcentage of asphaltene but the turpentine fraction becomes a smaller proportion of the total bitumen while the chloroform fraction becomes larger.

An investigation of the table of the percentage composition of the following varieties of asphaltum will confirm this statement:

No. 1. An average sample of land asphaltum from the island of Trindad.

No. 2. Altered or "aged" (iron pitch) Trinidad land asphaltum.

No. 3. Altered or "aged" Trinidad land asphaltum.

No. 4. An average sample of Trinidad lake asphaltum.

No. 5. An altered or "aged" Trinidad lake asphaltum.

No. 6. An altered or "aged" Trinidad lake asphaltum.

No. 7. An altered or "aged" (iron pitch) Trinidad lake asphaltum.

No. 8. Asphaltum from Montague Co., Texas.

No. 9. Turrellite from Uvalde Co., Texas.

No. 10. Asphaltum from near Ardmore, Indian Ter.

No. 11. Grahamite from Ritchie Co., W. Va.

No. 12. Scyssel asphaltic rock from Eastern France.

Sample.	Petrolene.	Turpentine fraction.	Chloroform fraction.	Asphaltene.	Total bitumen.	Ratio of chloroform fraction to total bitumen.	Organic matter not bitumen.	Mineral matter.
1	33.73	15.67	3.179	18.849	52.579	1 : 16	11.528	35.886
2	33.574	13.7	9.627	23.327	56.901	1 : 6	8.414	34.684
3	21.362	15.2	15.112	30.312	51.674	1 : 3	9.85	38.375
4	35.40	12.300	5.287	17.587	52.987	1 : 10	10.962	36.100
5	26.925	18.613	6.687	25.3	52.225	1 : 8	11.237	36.537
6	19.25	22.35	10.962	33.312	52.562	1 : 5	9.562	37.875
7	22.25	9.785	12.54	22.325	44.575	1 : 4	8.937	46.462
8	7.538	1.601	trace	1.601	9.139	....	....	90.861
9	8.786	3.267	trace	3.267	12.053	....	....	87.947
10	9.503	0.9905	trace	0.9905	10.4935	....	....	89.5065
11	49.959	17.458	32.583	50.041	100.00	1 : 3	....	....
12	7.486	3.945	0.371	4.316	11.802	1 : 31	....	88.198

I am not yet prepared to say that the turpentine fractionation of asphaltene, if made in the case of the asphaltum obtainable from

different parts of the world would indicate the relative "ageing" of the different varieties, but my experience with Trinidad Pitch inclines me to think that this will prove the case when such analyses are made. However, even if the turpentine determination should prove of no value as indicative of "ageing" processes in asphaltum, there is still a weighty reason why it should not be abandoned.

The marked physical difference between the turpentine and chloroform fractions would seem to indicate the probability of a chemical difference and I am sure that when an ultimate analysis of asphaltum has been made, as it will be in the near future, that turpentine as a solvent will be proven to have its place.

I am aware that some object to the use of turpentine because it is not pleasant to work with, particularly when it is boiling hot, but in scientific research we are seeking truth and not our own pleasure and convenience. If the cooperation of chemists engaged in the investigation of asphaltum could but be secured the solution of the problem would be a speedy one. But this may not be, so solvents are accepted or rejected at will with apparently no principle ruling in the choice. One chemist of wide reputation rejects chloroform and uses carbon disulphide as the final solvent in the extraction of bituminous matter.

I have analyzed many different varieties of American and foreign asphaltum and, with the exception of the Neufchatel, which is practically all petrolene, and the asphaltum from Texas and Indian Territory, all yielded more or less bituminous matter on treatment with chloroform after exhaustion with other solvents. Now, because the Neufchatel and a few other varieties need no chloroform for the extraction of bitumen, shall this solvent be stricken from our category ? rather let our scheme be so broadened as to be applicable to every variety of asphaltum the earth holds.

UNIVERSITY OF MICHIGAN.

DISCUSSION.

A. H. Sabin : This asphaltum business is one of a great deal of commercial importance. There are a great many things about it that we do not know ; I hope somebody here can tell us a few things.

In the first place asphalts are a very peculiar set of bodies. The most attention has been given of late years to Trinidad, because it has been used for paving purposes, and has been of immense commercial importance. It has generally been overlooked by the chemists who have worked on this line, that comparatively recently the commercial introduction of asphalts from other sources has been of great importance. Ordinarily chemists analyze either the Trinidad or Egyptian asphalts. The Egyptian asphalt is considered to be a representative of the high grade asphalts which are to be found in the East, while the Trinidad asphalt is a cheaper variety, very elastic, and contains a large amount of foreign matter. Commercially, as a matter of fact, the Egyptian asphalt is higher priced than the American, and so are all the Eastern asphalts. The fact has been known for a number of years that large deposits of asphalt are found in Utah and Colorado known as Gilsonite and Uintahite. These have been put on the market at such low prices that in St. Louis, I understand, Gilsonite is used in the paving trade. Gilsonite is an exceedingly pure asphalt. It is a very interesting substance, and it is hoped that future investigations will take into consideration the fact that these more recently discovered beds, which promise to be of more commercial importance than the Trinidad deposits, are practically inexhaustable. Some asphalt deposits are being developed in South America. We have the general statement made in Dana's Mineralogy, which so far as I can learn is based upon the well known investigations made long ago in France, and partly on some work chiefly in the line of checking results, which was done in the Sheffield Scientific School, that all petroleums contain more or less asphalt in solution, and that it is generally believed that asphalts are a sort of petroleum residue, and that the natural asphalts differ from the asphalts which are obtained as petroleum residues in being oxidized compounds. As near as I can find out that term "oxidized" is merely a conventional term. It means that the hydrogen has been removed, not that the oxygen has been added, although they show upon analysis that some oxygen is present. The chief difference apparently is that compounds containing hydrogen have escaped. The differ-

ence between hard and soft asphalts is just that difference that the mineral oils have been removed in some way or other from the asphalts and they are therefore hard; whereas some of them like the Trinidad have a considerable amount of mineral oily matter in them and are very elastic and well adapted to paving purposes. The presence of these ingredients, while it adds to their durability, detracts from their usefulness for other technical purposes, because mineral oil is comparatively easily removed by the action of the weather, while the hard asphalts not containing this volatile and soluble matter can be made elastic by being compounded with linseed oil and other substances, and in that way can be made immensely more permanent than elastic asphalts. This is inapplicable to paving, but it has large application. There is a good deal of commercial asphalt on the market under the name of Maltha, which was used as long ago as the time of Rliny. The name has been recently applied to asphalt from southern California. It is obtained in various degrees of hardness from a thick liquid to a solid, and is a good illustration of the so-called artificial asphalts. Of course, it is a natural product. Nothing has been done to it except the volatile portions have been distilled out of it. I should like to know whether these asphaltic constituents are present in all petroleums, or whether they are in some cases or in all cases produced by the action of high temperature upon the crude oil, and whether these differ from natural asphalt in oxidation or in what way?

Prof. Mabery: I have had some experience with asphalts in the way of observation, and to a certain extent experimentally. At Oil Springs, in Canada, a surface oil is found that is very heavy, with a specific gravity of 90, and in the vicinity of beds of asphaltic pitch. There is no question that there has been a change through the heavy surface oil into the asphalt. Some constituents of petroleum are very unstable; for example, at a temperature of 80°, *in vacuo*, a distillate was collected, which, after standing two years and then again distilled, decomposed into tar which could not be distilled without carbonization, doubtless the result of polymerization.

In regard to the origin of petroleum there is a great deal of

conjecture. So far as oxidation is concerned, the amount of oxygen contained in it is small. Recently we examined a product made from petroleum residue which resembles in some respects natural asphalt. It may be that some of you have heard of it under the name of Byerlyte. It is manufactured in this city. The process consists in taking the heavy oil after the burning oil is distilled, putting it into the still, passing in currents of air and applying a gentle heat to the bottom of the still during five or six days. Then the product is drawn off. It contains no fixed carbon. It resembles in some respects natural Gilsonite. So far as practical uses are concerned they are closely related. With reference to oxidation the quantity of oxygen does not appear to be very different from that in crude oil. As Mr. Sabin suggests, we cannot look upon oxidation in the production of asphalt as the introduction of oxygen, but rather as the removal of hydrogen, and that is doubtless related to certain features of polymerization. It seems to be a conversion of the unstable hydrocarbons into higher products. Concerning the composition of these products we know very little.

Other products have come under my observation which are on the market at the present time and used for insulators.

In some heavier sludges polymerization takes place when substances are formed closely resembling asphalt. There is a great field of investigation surrounding asphalt, but it is an exceedingly difficult subject.

The determination of water is an interesting question. It is practically impossible to remove water from petroleum by the ordinary methods. Ohio and Canada petroleum may stand for months, and when it is again distilled, water will appear to a considerable extent. Those pure hydrocarbons, which I showed last evening, can not be dried with calcium chloride. We found the moisture could only be removed by sodium, and after it is removed, upon exposure to the air, it reabsorbs moisture with great rapidity. Probably the same thing would apply to asphalt. Of course, in heating, the water will be removed, but if the products are again exposed to the air they will reabsorb the water. This question should be undertaken from the standpoint of thorough chemical investigation.

Mr. Sabin: These artificial asphalts have some very remarkable commercial differences from the natural asphalts. For example, they resist the action of sodium hydroxide. Sodium hydroxide seems to combine with almost all natural asphalts, but not with pitches or tars. In the same way for the purpose for which I use it, it is impossible to use it as asphalt, or in the way in which you can use any natural asphalt. You can not melt it alone without decomposition. It can be melted with other substances, such as rosin or some mineral oils. But it does not mix with the vegetable oils, such as linseed by itself. It is used very successfully as an insulator, as many of the pitches are. It has many useful and valuable qualities, which none of the asphalts have, especially that of resisting caustic alkali, but for many purposes it differs as widely from natural asphalt as if it were entirely and absolutely a different substance.

REVIEWS.

THE VALENCY OF OXYGEN AND THE STRUCTURE OF COMPOUNDS CONTAINING IT.

Hydrogen Dioxide.—In a recent issue of the Berichte der deutschen chemischen Gesellschaft[1] J. W. Brühl calls attention to the significance of recent work of Moritz Traube upon the structural formula of hydrogen peroxide. Traube found that when, in the electrolysis of water, the electrodes are separated by a diaphragm, no hydrogen peroxide forms. If now air be blown through the solution in contact with the cathode, hydrogen peroxide forms in quantity, presumably by the oxidation of the nascent hydrogen by the molecular oxygen of the air. Traube has also shown that when silver oxide is reduced to metal with formation of water and free oxygen, the latter comes from the peroxide, the oxygen of the water coming from the silver oxide, thus:

$$Ag_2\boxed{O+H_2}O_2 = Ag_2 + H_2O + O_2.$$

The constitutional symbol of hydrogen peroxide is usually written H.O.O.H. If this be correct we should expect it to unite with the olefines forming glycols by direct addition. Glycols seem not to be formed in this way, except in the case of

1 28, 2847.

ethylene glycol, which, according to Carius,[1] is formed by adding ethylene to hydrogen peroxide in "verhältnissmässig sehr kleine Mengen." But even if this reaction takes place it would not prove the correctness of the above structural formula since glycols are formed by acting on the olefines with potassium permanganate. The formation of hydroxides by the action of hydrogen peroxide on the metals, such as zinc, is inconclusive for the same reason.

Neither does the formation of salts, such as barium dioxide from hydrogen peroxide prove anything, since we know many acids which contain no hydroxyl.

Because of the fact that in all its decompositions, molecular and not atomic oxygen, was liberated, and of its formotion from molecular oxygen and atomic hydrogen, Traube wrote the symbol:

$$H.O{:}O.H.$$

Additional interest attaches to this question since Wolffenstein has shown[2] that hydrogen peroxide may be concentrated and obtained by distillation in a vacuum as an explosive, nearly anhydrous substance.

Spring has recently shown[3] that thick layers of hydrogen peroxide have a bluer color than water, and since ammonium iodide is colorless, and NH_4I_3 and NH_4I_4 are green or violet, this indicates the possible presence also of molecular oxygen in the peroxide.

From his determination of its specific heat Spring concludes that the elements H_2 and O_2 in combining have used only a part of their potential energy, which is more nearly in harmony with Traube's formula than with that commonly accepted.

Brühl has now[4] determined the index of refraction of the pure nearly anhydrous substance and the specific gravity, and from these he has calculated the specific refraction and dispersion and the molecular refraction and dispersion. The molecular refraction and dispersion is found to be:

$$M_a = 5.791.$$
$$M_{Na} = 5.817.$$
$$M_\gamma - M_a = 0.136.$$

If we subtracted from the corresponding constants for water, the constants for the hydrogen atom, the values for the latter being nearly the same as in its compounds, we get the following:

[1] *Ann. Chem.* (Liebig), 126, 209.
[2] *Ber. d. chem. Ges.*, 27, 3307.
[3] *Ztschr. anorg. Chem.*, 8, 424; 9, 205.
[4] *Loc. cit.*

	M_α.	M_{Na}.	$M_\gamma - M_\alpha$.
HOH	3.69	3.71	0.09
H	1.10	1.05	0.04
HO	2.59	2.66	0.05

This would give, doubling these values for hydrogen peroxide:

	M_α.	M_{Na}.	$M_\gamma - M_\alpha$.
H.O.O.H	5.18	5.32	0.10

These values are, however, much smaller than those observed for hydrogen peroxide, (see above). The easiest explanation of the fact that the spectrometer constants of hydrogen peroxide are considerably larger than would correspond to the symbol H.O.O.H, lies in the assumption of multiple union between the oxygen atoms. This would necessitate the assumption of multiple union in ordinary oxygen, and while this is not proven, it is indicated by the recent work of Olszewski and Witowski,[1] and especially by the work of Liveing and Dewar[2] on liquid oxygen. If we compare the optical equivalents of two atoms of oxygen in water with the constants of molecular oxygen, we get:

	M_α.	M_{Na}.	$M_\alpha - M_\gamma$.
2O in water	2.968	3.212	0.036
O_2 as molecular oxygen, liquid	3.958	3.964	0.069
O_2 as molecular oxygen, gaseous	....	4.09	....

This shows that the optical constants of the molecular oxygen are considerably greater and the dispersion double that of the oxygen in water. This is, however, the best criterion of multiple union of the atoms.

But if in hydrogen peroxide the oxygen atoms are united by multiple union, fewer valencies must be concerned than in molecular union.

If this conjecture be granted, we should find the oxygen constants from hydrogen peroxide somewhat smaller than the molecular oxygen, and this is the case, as is seen below:

	M_α.	M_{Na}.	$M_\gamma - M_\alpha$.
Oxygen in water (2O)	2.968	3.212	0.036
Oxygen, O_2, in hydrogen peroxide	3.591	3.717	0.055
Oxygen, O_2, molecular, liquid	3.958	3.964	0.069
Oxygen, O_2, molecular, gaseous	....	4.09	....

If we assume Traube's symbol for hydrogen peroxide to be correct, we must call oxygen trivalent, for which we have no

[1] Bulletin Acad. Cracovie, Oct. *1891*, 341.
[2] Phil. Mag., 37, 268.

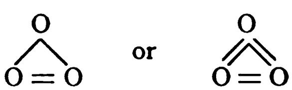
warrant; neither is any member of the oxygen group of the periodic system known with a valence of three.

On the contrary, sulphur, selenium and tellurium are bivalent and quadrivalent, and several compounds indicate the quadrivalence of oxygen, such as Rose's quadrantoxides, (Ag_4O), but especially the compound of Friedel[1] $HCl(CH_3)_2O$. If it be granted that oxygen may be quadrivalent, we may then write hydrogen peroxide:

$$H.O{:}O.H.$$

All the known properties of hydrogen peroxide; its formation from nascent nydrogen and molecular oxygen; its decomposition by nascent oxygen; its endothermic decomposition are explained by this structural formula.

Constitution of Ozone.—On the assumption of the quadrivalence of oxygen, the symbol of ozone may be either



No data are yet at hand sufficient to decide this question.

Constitution of Carbon Monoxide.—For many years carbon monoxide has remained as the single illustration of the bivalence of carbon. If we assume that oxygen is quadrivalent, however, this difficulty at once disappears. The spectrometric behavior of carbon monoxide favors this view. Brühl has shown[2] that carbon monoxide has the following molecular refraction:

	M_{Na}.
Found	5.04
Calculated for C:O	4.79

This small difference is, however, many times greater than the possible experimental error.

The assumption of the structure C:O for carbon monoxide involves the assumption of unsaturated oxygen in numerous carbon compounds; at least in those containing an uneven number of carbon atoms; but we have also many sulphur and nitrogen compounds in which these atoms are bivalent and trivalent respectively.

The Constitution of Water.—In another paper Brühl considers[3] the result of this new view upon the constitution of water. It is known that in aqueous solutions of salts of strong acids and bases, the observed alteration of the freezing-and boiling-points is nearly double the normal amount deduced from van't Hoff's

1 *Bull. soc. Chim.*, 24, 160, 241.
2 *Ber. d. chem. Ges.*, 24, 663.
3 *Ber. d. chem. Ges.*, 28, 2866.

equation. We know also that Arrhenius has accounted for this by supposing that in such solutions the salts are decomposed into their ions.

It is known, further, that many organic substances, such as the fatty acids, oximes, alcohols, etc., form double molecules or molecular complexes when dissolved in hydrocarbons, chloroform and carbon disulphide, and that these complexes are broken up when these substances are dissolved in water, and to a certain extent also when dissolved in alcohols, ethers, esters, ketones and phenols. The latter class of solvents are to a certain extent also ionizing, since when saturated with hydrochloric acid they act as conductors, while solutions of hydrochloric acid in benzene and other hydrocarbons are non-conductors.

Why water so far surpasses other solvents in its power to allow of this dissociation is not known, but the explanation is easily found if we write water as an unsaturated compound giving oxygen four bonds, thus:

$$H \cdot \overset{\cdot}{\underset{\cdot}{O}} \cdot H.$$

In fact the properties of water indicate almost with certainty that it is unsaturated, for nearly all substances have a tendency to unite with it—are hygroscopic. Numerous hydrates and compounds with water of crystallization exist, and, finally, water is the universal solvent. The supplementary valencies of the quadrivalent oxygen are evidently the cause of the formation of the ions, and the molecular aggregates the reason of the dissociating power of the water.

This notion receives further support when we remember that all those organic solvents which are known as good dissociation media contain oxygen—ethers, alcohols, esters, ketones, phenols, urethanes, etc.—while those free from oxygen, such as the hydrocarbons, chloroform, carbon disulphide, carbon tetrachloride have little or no power to cause dissociation.

EDWARD HART.

THE HISTORY OF ELECTRIC HEATING APPLIED TO METALLURGY.[1]

Sir Humphry Davy is justly regarded as the father of dry electro-metallurgy. After making full allowance for the unusual facilities at his command, it still remains that his intelligent, faithful and extended use of his facilities is worthy of the utmost honor.

[1] Read before the Washington Section, Dec. 12, 1895.

It often happens, however, with epoch-making events that a close search reveals previous indications, so in this case it is found that not only was Davy's dry work preceded by a course of wet electro-chemical experiments, as pointed out by Davy himself, but also an important contribution to dry electro-metallurgy had been made long previous to Davy, and that this even preceded the first observed decomposition of water by the current.

In 1795 a Dutch book of 396 pages was published at Haarlem by Martinus Van Marum, entitled "Second Continuation of Experiments by Means of the Teyler Electric Machine." I have not seen the original book, but various notices[1] of it appeared in the Journals at the time. From these it appears that Van Marum was a thoughtful and exhaustive investigator. His investigations took a wide range and included much outside our title. He, however, not only observed the heat produced by the passage of the current, but he actually measured it. In one instance the temperature of his apparatus, designed for measuring this effect, rose from 61° to 88° in three minutes, and to 112° in five minutes. He volatilized phosphorus in a tube and [illegible] proved it to be "phosphor gas." He investigated the suitability of metals for lightning rods and determined that copper was [illegible] as twice as good as iron. He oxidized metals by the current and performed various melting experiments. He had a scale to [illegible] to measure the current and at twenty-four 100 feet of iron wire, $\frac{1}{24}$ [illegible] $\frac{1}{40}$ inch in diameter, melted, while 104 feet melted and separated into globules. He also melted longer pieces, but concluded that such melting tests were not worth the while. Sixty feet of No. 11 wire, $\frac{1}{150}$ in diameter, melted at 24.5, but at the same point thirty-six feet of No. 1 wire glowed its full length, one-half being quite blue and the rest slightly oxidized. Quartz was split up and slightly melted.

Having oxidized the metals by the current, he conceived the idea that the oxides could be again reduced to the metallic state by the application of larger amounts of the current. It does not appear that he actually used electrically produced oxides to test this idea, for he not only did test it, but also actually collected and tested the gas given off.

His furnace, if I may so call it, was a glass tube with platinum electrodes. In this he put his oxide and passed the current with the following results: Red lead gave lead on the surface of the tube in a few moments that could be gathered up, and in twenty minutes he collected three-quarters cubic inch of gas. White lead gave lead in smaller amounts. Tin oxide gave no metal.

[1] *Aellern J. der Physik.*, 4, 1; 6, 37, 360; *Neue J. der Physik.*, 3, 1; *Pog.*, 1, 68, *et al.*

Red oxide of iron gave no metal. Red oxide of mercury gave mercury and a little gas. He proved that the gas given off was oxygen and credits the decomposition to heat.

In a lecture delivered during the latter part of his life, Sir Humphry Davy gave a history of electro-chemistry, from which I take the following statements :

"The true origin of all that has been done in electro-chemical science was the accidental discovery of MM. Nicholson and Carlislie, of the decomposition of water by the pile of Volta, April 30th, 1800." "In the month of September, in the same year, I published my first paper on the subject of galvanic electricity in Nicholson's Journal, which was followed by six others, the last of which appeared in January, 1801. In these papers I showed that oxygen and hydrogen were evolved from separate portions of water, though vegetable and even animal substances intervened, and conceiving that all decomposition might be polar."

"In 1804, MM. Heisenger and Berzelius stated that neutro-saline solutions were decomposed by electricity, and the acid matter separated at the positive, and the alkaline matter at the negative poles; and they asserted, that in this way muriate of lime might be decomposed; and drew the conclusion that nascent hydrogen was not, as had been generally believed, the cause of the appearance of metals from metallic solutions."

"In 1805 various statements were made, both in Italy and England, respecting the generation of muriatic acid and fixed alkali from pure water. The fact was asserted by MM. Pachioni and Peele, and denied by Dr. Wallaston, M. Biot, and the Galvanic Society at Paris."

"It was in the beginning of 1806 that I attempted the solution of this question, and after some months labor, I presented to the Society the dissertation to which I have referred in the beginning of this lecture. Finding that acid and alkaline substances, even when existing in the most solid combinations, or in the smallest proportions in the hardest bodies, were elicited by voltaic electricity, I established that they were the result of decomposition, and not of composition or generation; and, referring to my experiments of 1800, 1801, and 1802, and to a number of new facts, which showed that inflammable substances, and oxygen, alkalies, and acids, and oxidable and noble metals were in electrical relation of positive and negative, I drew the conclusions that the combinations and decompositions by electricity were referable to the law of electrical attractions and repulsions."

It is curious that Davy should have overlooked the very early work of Van Marum.

From this work Davy naturally passed to the question of decomposing the fixed alkalies by the current. It is not so much to the work itself, beautiful as it was, to which I wish to direct attention now, as it is to the fact that Davy not only did a vast amount of work and secured wonderful results, but he also clearly pointed out the principles involved, and at this early date enunciated the conditions of successful operation upon which the modern practical applications of electric heat to metallurgical operations rest.

He has so plainly traced the history of his work and pointed out the underlying principles that I cannot do better than quote his own words. He says:[1]

"In the first attempt that I made on the decomposition of the fixed alkalies, I acted upon aqueous solutions of potash and soda, saturated at common temperatures by the highest electrical power that I eould command, . . . though there was a high intensity of action, the water of the solutions alone was affected, and hydrogen and oxygen disengaged with the production of much heat and violent effervescence.

"The presence of water appearing thus to prevent any decomposition, I used potash in igneous fusion,

"By this arrangement some brilliant phenomena were produced.

"I tried several experiments on the electrization of potash rendered fluid by heat, with the hopes of being able to collect the combustible matter, but without success, and I only attained my object, by employing electricity as the common agent for fusion and decomposition."

Here is the clearest kind of statement of the value of using the current for the double purpose of fusing the material to be acted upon, and for decomposing it. In modern practice this principle was used, notably in the Heroult process of smelting aluminum alloys, and is now used in the successful processes of extracting pure aluminum, such as the Hall process in the United States and its equivalents abroad.

Continuing, Davy said:[2]

"The substance was likewise produced from potash fused by means of a lamp, in glass tubes confined by mercury and furnished with hermetically inserted platina wires by which the electrical action was transmitted."

This may be considered as a hint at electric heating under pressure, as proposed later by Werderman, de Grousilliers and Menges.

1 Works of Sir Humphry Davy, 5, 58, 59, 60.
2 Works of Sir Humphry Davy, 5, 61.

And in regard to the production of sodium he said:

"Soda, when acted upon in the same manner as potash, exhibited an analogous result; but the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces."

In modern practice the benefits to be derived from alloying the separated metals, at the moment of their reduction, with another metal, is an essential element of the Cowles and Heroult aluminum alloy processes, and also of various processes of the electrolytic production of caustic soda, notably Castner's process. Here too Sir Humpry Davy was early in the field with both work and word.

After describing various obstacles and the conditions necessary in decomposing the alkaline earths as an essential to success, he says:[1]

"Or of combining them at the moment of their decomposition by electricity in metallic alloys, so as to obtain evidence of their nature and properties.

"Barytes, strontites and lime, slightly moistened, were electrified by iron wires under naphtha, by the same methods and with the same powers as those employed for the decomposition of the fixed alkalies.

"I had found in my researches upon potassium, that when a mixture of potash and the oxide of mercury, tin or lead was electrified in the Voltaic circuit, the decomposition was very rapid, and an amalgam or alloy of potassium was obtained; the attraction between the potassium and the common metals apparently accelerating the separation of the oxygen.

"The idea that a similar kind of action might assist the decomposition of the alkaline earths, induced me to electrify mixtures of these bodies and the oxide of tin, of iron, of lead, of silver, and of mercury, and these operations were far more satisfactory than any of the others.

"These experiments were made previous to April, 1808.

"The earths were slightly moistened, and mixed with one-third of oxide of mercury, the mixture was placed on a plate of platina, a cavity was made in the upper part of it to receive a globule of mercury, of from fifty to sixty grains in weight, the whole was covered by a film of naphtha, and the plate was made positive and the mercury negative, by the proper communication with the battery of 500.

"The amalgams obtained in this way were distilled in tubes of plate glass, or in some cases tubes of common glass."

In modern practice the crucible or containing vessel is usually

[1] Works of Sir Humphry Davy, 5, 104, 107, 108, 111.

used as one of the electrodes, generally the negative. Sir Humphry Davy did the same, but like Siemens, made his crucible the positive pole, and in this particular case used external heat for fusing his charge. He says:[1]

"I fused a mixture of one part of silex and six of potash in a platina crucible, and preserved the mixture fluid, and in ignition over a fire of charcoal; the crucible was rendered positive from the battery of five hundred, and a rod of platina, rendered negative, was brought in contact with the alkaline menstruum.

"I tried similar experiments with mixtures of soda and alumina, and soda and zircone, and used iron as the negatively electrified metal."

The work of Sir Humphry Davy was followed by the work of Children, 1809–1815. In his first communication[2] he dealt mainly with the difference in the results produced by a battery consisting of a small number of large plates, and one consisting of a large number of small plates. The most interesting part of this paper, in tracing the history of metallurgical electric heating, is experiment 6, which is undoubtedly the first description of the passage of an electric current through a mixture of ore and resistance material, although it yielded no results. This principle was afterwards very successfully employed by the Messrs. Cowles. In this experiment of Children a mixture of sulphate of barium, red oxide of mercury and clay was submitted to the action of the current.

In his second paper[3] he described his work upon the relative conductivity of wires of various metals, and found that elevation of temperature affected the result.

He subjected various oxides, mostly of the rarer metals, to the action of the current, with varying results, some simply fused more or less, some were also reduced to metal. He also tried some experiments in simply melting.

His crucible consisted of a bit of boxwood charcoal, hollowed out on top with a little mercury in the cavity, serving as one electrode; upon this was placed a piece of the oxide; the other charcoal electrode was then brought near.

In this paper is also described Pepys celebrated experiment to determine that the diamond was really carbon. For this purpose a soft iron wire was bent and split by a saw; into the split some diamond powder was placed and bound in by fine wire, and the whole covered by leaves of talc. The current was then passed through the wire. The heat produced was not high, but the iron was carburized.

1 Works of Sir Humphry Davy, 5, 119–120.
2 Phil. Trans., 1809, 32.
3 *Ibid.*, 1815, 363.

From this time on for over thirty years nothing seems to have been done in electric heating, although there were a few applications of the current to metallurgical processes in connection with external or other heat, such as the English Patents No. 9,946 of 1843, to A. Wall, for the use of the current in the blast furnace, and No. 10,362 of 1844, and No. 10,684 of 1845, to Napier for treating copper ore by the current in crucibles.

In 1848 and 1849 Despretz[1] published a series of articles in which he described the effect of combining the heat from three different sources, the electric current, the blowpipe and a burning glass. He clearly illustrates the difference between temperature and quantity of heat, the great difference there may be in the temperature of the source of heat and the temperature attained by the material heated, and that the loss of heat from the material heated, may be supplied by a source of heat at a comparatively lower temperature and allow a higher temperatured source of heat to exert its full heating effect. Thus on heating magnesia by the current at his command it simply became pasty, but on adding to this the heat of the burning glass it immediately volatilized in white fumes.

He determined that it is easier to volatilize carbon than to melt it; also that time, mgnesia and oxide of zinc hehave in the same way. He melted alumina to a transparent glass; he also melted titanic acid in various forms, oxide of iron and disthen.

He suggested the use of the current for melting metals practically, and melted eighty grams of palladium and 250 grams of platinum.

In his last communication Despretz described an arrangement in which a quantity current was passed through his crucible while a separate series current was passed through the contents.

In 1853 an English patent No. 12,772 was granted to Staite & Petrie, in which the current was applied to the treatment and fusion of iridium.

In 1849 an English patent No. 5 was granted to Watson & Prosser for the use of the current in converting iron into steel by which the time of convertion was to be shortened, and the quality of the steel improved. In one case the current was passed through the enclosing trough, and in another the poles were put into the cementing material surrounding the bars. These propositions seem to resemble some of the modern ideas of producing heat, but it is not clear that Watson & Prosser used sufficient current to produce any considerable heating effect.

Although I have not yet been able to locate the exact date, I mention here the Grove furnace which has been called the pro-

[1] *Compt. Rend.* 28, 755; 29, 48, 545, 709; 30, 369.

the incandescent furnace. It consisted of a carbon set in mercury, making the current connection, while :r served as the other electrode. It was mentioned in ıiere Electrique, **19**, 350, and Scientific American Sup., .4, 1886.

come now to the first real attempt to employ the electric ıt to heat and act upon a charge of ore in a practical way. ound in the invention of M. Pichon, patented in France, :h 16, 1853, covered by English patent[1] No. 700 of 1853. ıis process iron or other ores are mixed with carbon and ¿en down between two or more pairs of electrodes through ıch the current is passing, when it melts, and after which it ›ps into an externally heated receptacle below.

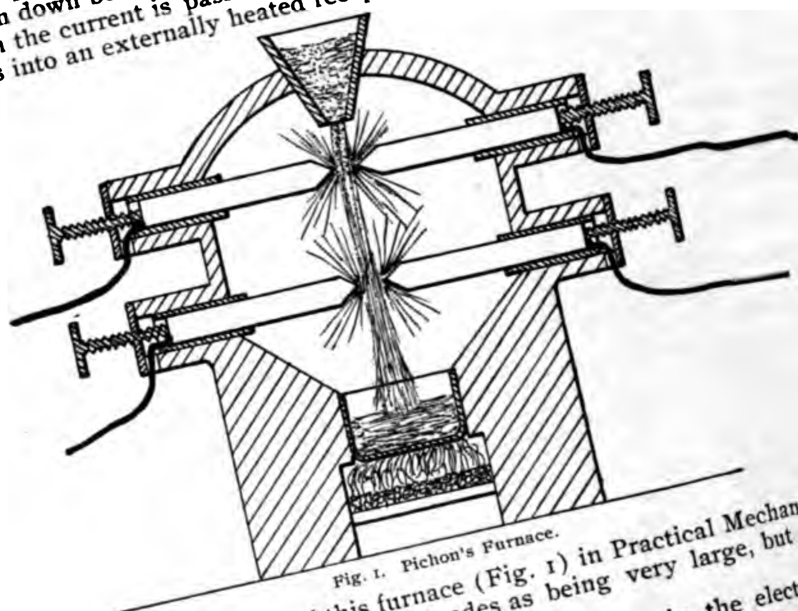


Fig. 1. Pichon's Furnace.

The description of this furnace (Fig. 1) in Practical Mechanics Journal speaks of the electrodes as being very large, but I think that feet should be read inches.

In 1854 Duvivier[2] placed a piece of disthen in the electric flame and produced globules of metal.

There is another long break after 1854 in our subject, strictly speaking, although there were many metallurgical proposition in which the current was employed, but they were either w processes, or else flame heat was employed.

1 See also *Practical Mechanics J.*, 6, 257, and Dingler, 131, 415.
2 *Compt. Rend.*, 38, 1066.

In 1866 Le Roux[1] published an exceedingly interesting and suggestive, but all too brief, communication upon the action of the arc upon lime and strontia. He decomposed lime and strontia in the arc and studied the reactions spectroscopically. He determined that the metals calcium and strontium were reduced, and carefully distinguished between the spectrum of the metals themselves and the spectrum of the white light resulting from the incandescence of the oxides. He asks the questions: Is the separation of the metals the result of electro-chemical decomposition? Is it due to vapor of carbon? Is it due to dissociation from heat alone? But he does not answer them.

We have seen that up to this time considerable work of a scientific character had been done from time to time in the field of dry electro-metallurgy, and that some suggestions at least had been made for the practical application of the current in this field. Undoubtedly, however, the cost of the current at this time was prohibitive. In looking over the field we can see the germs of modern processes, and easily imagine that if the early workers had been supplied with cheap current they would have carried their work very much farther, and developed practical electric metallurgical processes of value, but it remains as a fact that they did not have cheap current, and did not invent modern electric metallurgy.

With the development of the dynamo in the seventies came a wave of activity in the application of the current to metallurgy in the late seventies, and early eighties.

Before considering this growth in detail it is well to look at the advantages to be derived from the current as a heating agent. In doing this a sharp distinction between quantity of heat and degree of temperature should always be kept in mind. Unfortunately these terms are often used, even by persons who really know better, and who thereby mislead those who do not know better, as if they were synonymous. This is not at all the case. We may have an enormous quantity of heat developed at a low degree of temperature of which the pile of rotting apples is the old and familiar example. On the other hand, we may have a very high temperature developed by a small quantity of heat. A good blowpiper can melt fine platinum wire in a small blowpipe flame. While the combustion of a given quantity of fuel will always supply the same quantity of heat the temperature developed may vary enormously. When we carry this consideration farther and apply it to the practical application of heat, this for difference becomes much more marked and pronounced. For instance, a mixture of iron ore and carbon may be supplied with any quantity of heat at a low temperature without reduc-

[1] *Compt. Rend.*, 30, 1150.

ing the metal; or a mixture of bar iron and carbon may be heated indefinitely to a low temperature without producing steel, but once the proper degree of temperature is reached the required reactions take place. On the other hand, the proper temperature once attained, a sufficient quantity of heat at the right temperature must be supplied to carry on operations. While the good blowpiper can readily melt a fine platinum wire in his flame yet he cannot even soften a stout laboratory rod of platinum.

In practical work we are farther limited by materials of construction, their fusibility, their heat conduction and radiation.

The temperature attainable by ordinary combustion is limited by the temperature of dissociation of carbon and oxygen, which has been put at 2500° to 2600° C., but at such temperatures combustion is slow and losses of heat large, so that the practically attainable flame furnace temperature is probably about 1800° to 2000° C., while the practical oxyhydrogen blowpipe temperature may be several hundred degrees higher, but where the flame must not come in contact with the materials under treatment, and the heat must pass through the walls of crucible or muffle, we must be content with a very much lower temperature.

With the electric current the conditions are changed. The first and most striking factor is the enormous temperature that can be both experimentally and practically reached. What the maximum temperature attainable may be has not yet been established, but temperatures about 3800° C. have been measured by Moissan and Violle. The second factor is that the heat can be developed right at the point where it is utilized, and the losses reduced to the minimum. This is especially advantageous in replacing muffle and crucible heating, as is also the fact that the heat is secured without the introduction of enormous quantities of products of combustion. Again the temperature is under most perfect control, and can be adjusted with the utmost nicety. There are also minor advantages in the cleanliness and compactness of the operations.

It remains, however, that the cost of the current limits its practical application even now to a few special cases, and this is likely to remain so until the dream of the electrician of converting coal directly into current be realized.

In 1875[1] an English patent, No. 4,043, was issued to G. L. Fox for heating a crucible by the heat generated by resistance to the passage of the current, but curiously enough his resistance material was placed outside his crucible, and the heat had still to pass through the walls of the crucible.

In 1878 a voluminous French patent, No. 122,227, was issued

to M. Repieff, in which arrangements of electrodes for electric furnaces are shown. In the electric light part of his patent he also uses oxides to color his light.

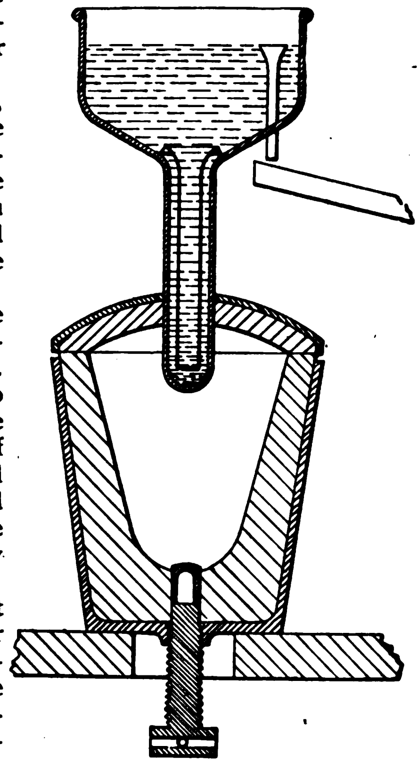


Fig. 2. Siemens' Furnace.

In 1878 an English patent, No. 4,650, was issued to Clarke and Smith for producing ammonia by passing a mixture of nitrogen and hydrogen through sufficiently prolonged white heat produced by the electric arc

The next electric fùrnace was that described in the celebrated English patent, No. 2,110, of May 27th, 1879, to C. W. Siemens. This may be said to inaugurate the era of electric furnaces proper, and to be the first real hearty and systematic attempt to make practical use of heating by the current.

As described in the patent with all its attendants of water cooled electrodes and regulating devices it is a formidable and elaborate piece of apparatus, but divested of its accessories its real operating parts become simply a crucible provided with two electrodes, arranged either vertically (Fig. 2) or horizontally (Fig. 3), through which the current passes.

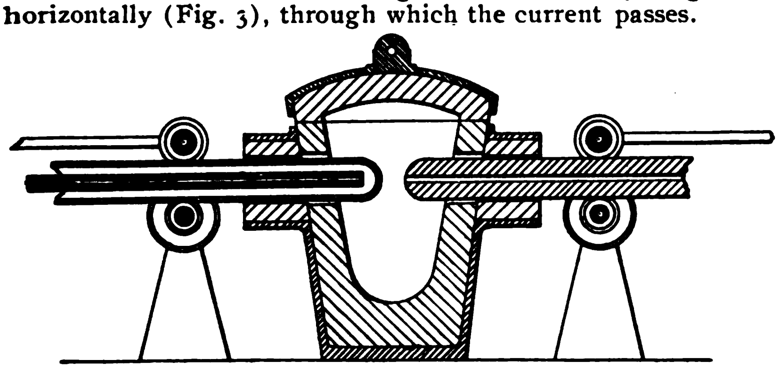


Fig. 3. Siemens' Furnace.

This apparatus was described and exhibited in actual operation before the Society of Telegraph Engineers[1] and the British Association.[2] The descriptions and exhibitions were confined for the most part to simple melting operations, although some attempts to saturate iron with carbon are described. It does not appear that Siemens ever used his furnace for the reduction of metals, although the article in *Iron* suggests that it might be so used. The death ot Siemens undoubtedly cut off work in that direction with this apparatus.

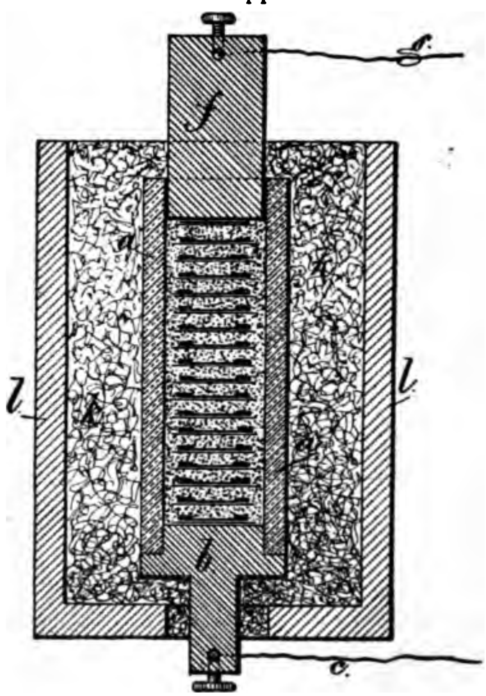


Fig. 4. Ball and Guest's Furnace.

In 1881 a United States patent, No. 236,-478, was issued to Ball and Guest for an electrical carbonizing apparatus (Fig. 4) to produce carbons for the electric light. The articles to be carbonized are placed in a pile within a case and are surrounded by pulverized carbon. The case is then brought into the circuit and the contents thereby heated. A portion of the current passes through the carbon packing.

In 1881 an English patent, No. 304, was issued to Werdermann for preparing carbon from sugar, which was then subjected in a mold to a white heat by the passage of the current, for use in electric lamps. In the same year silicon was to be heated by the current to prepare it for use in electric lamps, French patent, No. 144,317.

The Belgian patent, No. 144,387, of Aug. 13, 1881, described a special form of furnace with onè or more pairs of electrodes to be forced forward by springs. The furnace was calcined magnesia mixed with metallic oxides.

In the Engligh patent, No. 3,757, of 1882, Werdermann pro-

[1] *J. Soc. Tel. Eng.*, 9, 285.
[2] *Chem. News*, 46, 163; see also *Iron* Supplement, 1880, p. 424.

posed to heat silicon under pressure by the passage of the current.

At the Washington meeting of the American Institute of Mining Engineers, in February, 1882, in discussing the paper of Mr. Keith on the application of electricity to mining and

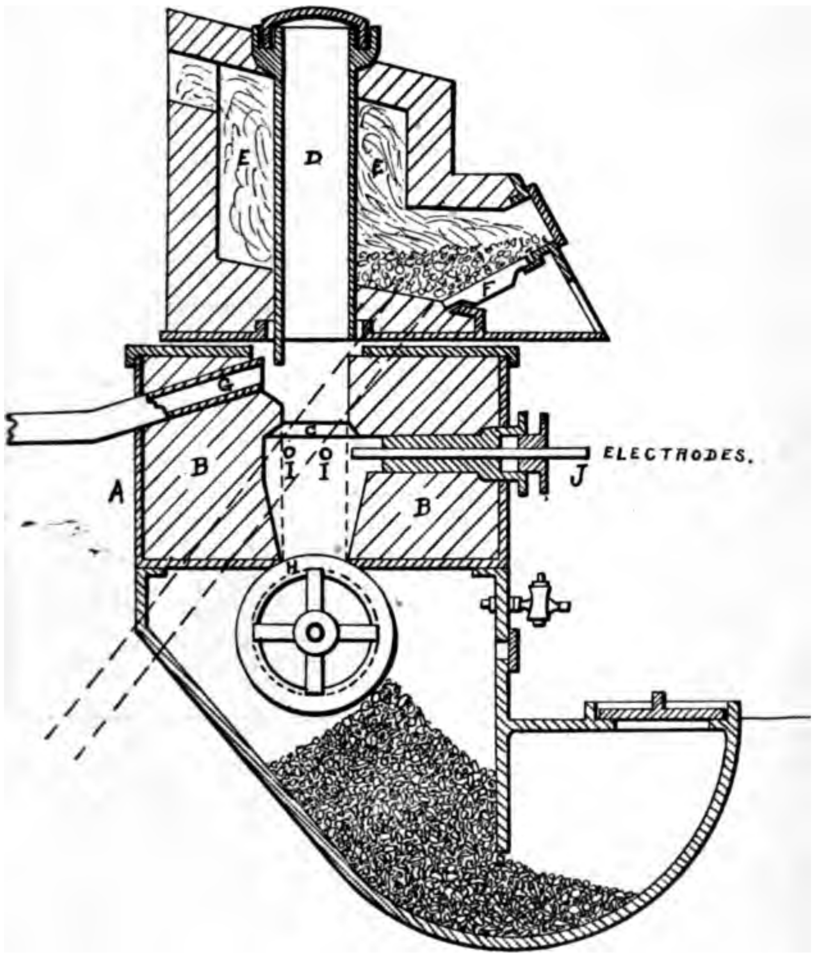


Fig. 5. Faure's Furnace.

metallurgy, Mr. H. M. Howe[1] briefly outlined a process which should have been developed into a successful commercial process. He said :

[1] Trans. Am. Inst. Min. Eng., 10, 317.

"The aluminous compound is placed in a carbon crucible, which is connected as the cathode of an electric current of great intensity. A voltaic arc is then thrown across from another electrode against this carbon crucible, the current thus first melting and then decomposing the aluminous compound, and metallic aluminum being deposited on the sides of the crucible."

In 1880–82–83–84 a series of patents[1] was issued to M. C. A. Faure, which has attracted considerable attention; more perhaps from their suggestiveness than from theii actual contents. As described in the English patent, No. 6,058, of 1882, the process was designed for the reduction of sodium, and the furnace (Fig. 5) consisted of a tube in which the charge was first heated by an external fire. It was then passed into a chamber provided with electrodes for the passage of the current where it

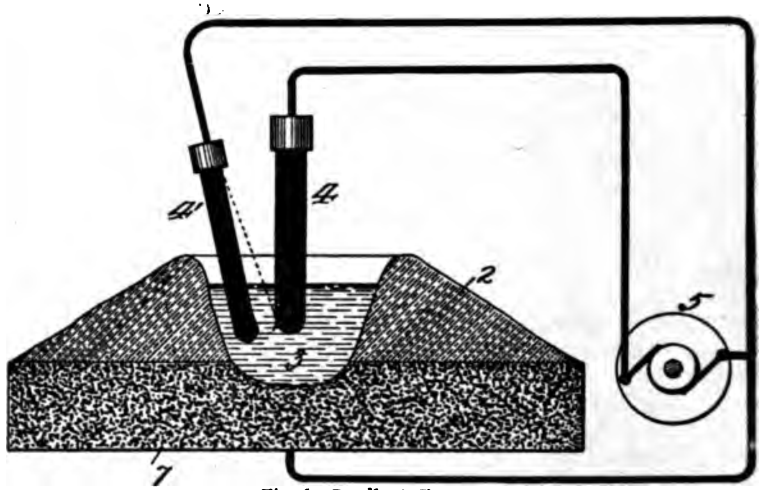


Fig. 6. Bradley's Furnace.

was intensely heated. Below was an automatic discharge for the refuse. There were also suitably condensing arrangements.

Chronologically considered, the United States patents to C. S. Bradley may be considered here, since the fundamental application was filed in February, 1883, although the patents were not issued for about nine years.[2] In these three patents (Fig. 6) the claims are drawn to cover three points. Using an unfused portion of the charge itself to enclose and contain the bath of fused material. Using the current for the double purpose of

[1] French patent No. 139,188. English patent No. 6,058, of 1882, and 5,489 of 1883, and Belgian patent No. 63,385.

[2] United States patents, No. 464,933, of Dec. 8, 1891; No. 468,141, of Feb. 2, 1892, and No. 473,866, of 1892.

fusing and decomposing the charge. Using a downwardly projecting blowpipe, or other flame, to supply a portion of the heat.

A United States patent, No. 282,964, was issued to Delaplaine, Hendrickson, and Clamer, in 1883, for melting the tin off from tin scrap by the current.

When, in 1885–86, the simple and beautiful process of Messrs. E. H. and A. H. Cowles' was announced, both the scientific and practical worlds were surprised and intensely interested, and a revolution in high heat metallurgy seemed imminent, particularly in the metallurgy of aluminum, but later developments have not fulfilled the early promises in general metallurgy, and aluminum metallurgy has now passed out of the field of high heats.

This process consists in mixing the ore to be reduced with a so-called resistance material (which for practical reasons was carbon) and then passing the current through. The current generated a very high heat and difficultly reducible oxides were reduced to metal. In the case of aluminum the reaction went a step farther, and the reduced metal combined with the carbon and formed a carbide of aluminum.

The generation of the heat was attributed to the passage of the current through the resistance material. This was not altogether so, but the high heat was generated by the passage of the current from particles of the charge to other particles, in other words, by dividing up the current into innumerable small arcs, and the great advantage of the process lies in evenly distributing the heat of a large arc through a considerable space, through which the material to be acted upon is distributed.

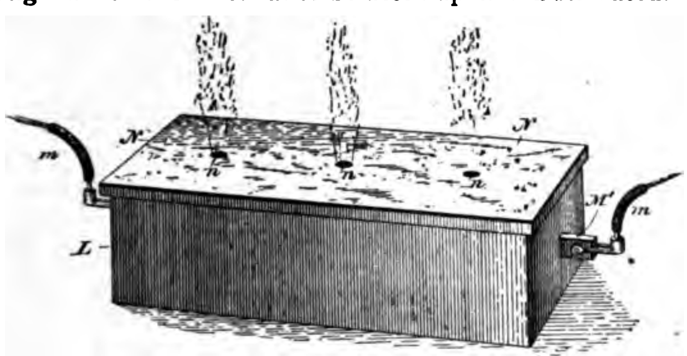


Fig. 7. Cowles' Furnace. (Outside).

The furnace (Fig. 7) consisted of an outside case of brick

[1] United States patents Nos. 319,795; 319,945; 324,658 and others. Also foreign patents. The Cowles process was widely described. Proc. A. A. A. S., 24, 136; Trans. A. I. M. E., 14, 492; *J. Franklin Inst.*, 121, 111, and 122, 51 and 273; *J. Soc. Chem. Ind.*, 5, 206; *Mont. Sci.*, *1885*, p. 1288, and *1886*, p. 1032, Industries, Vol. 8, p. 273, 294, and elsewhere.

work, lined on the inside with carbon, then the charge containing the ore and carbon was put into the centre in contact with the electrodes, the charge was covered with carbon and a perforated cover placed over all.

By this process silicon, potassium, sodium, magnesium, calcium, chromiun, and titanium, as well as aluminum, were produced, but on account of so much of the aluminum combining with carbon, it became necessary to introduce an alloying metal

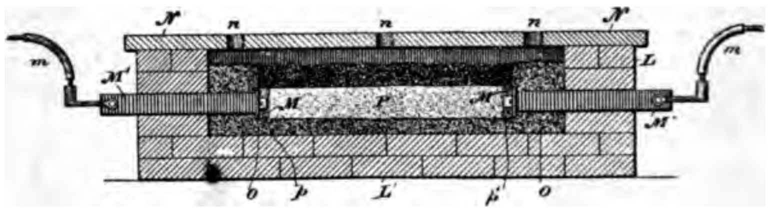


Fig. 7. Cowles' Furnace. (Inside).

into the charge. This was usually copper or iron. By this process the price of aluminum in alloys was very largely reduced but no considerable amount of the pure metal was ever produced.

In 1886 a United States patent, No. 335,499, was issued to Bradley and Crocker, in which the current was used to heat the charge, and was divided into two portions, one part passed through the walls of the retort, and another passed through the charge.

In 1887–88 a series of patents[1] was granted to M. P. L. T. Heroult, in which alumina was melted by the passage of the current and then electrolyzed with molten copper, or iron, as the cathode with which the separated aluminum alloyed.

The furnace (Fig. 8) was a suitable containing vessel of carbon to which the negative wire was attached. The positive electrode was of carbon. In running the furnace copper or iron was first put in and melted by the current, then alumina was added, which was also melted, and then electrolyzed by the current. More alumina and copper, or iron, were added from time to time, and the resulting alloy was tapped out periodically.

This was a very promising high heat alloying process, but it, as well as the Cowles process, was superseded in the aluminum field by the Hall process of producing the pure metal, of which it is only necessary to say here that in this process the charge is both melted and electrolyzed by the current, but the fact is to be emphasized that only a comparatively low temperature is required.

[1] French patent No. 170,003. Belgian patent No. 77,100. English patent No. 7,426 o[illegible] 1887. United States patent No. 387,876. See also Richards Aluminium, 2d ed., p. 36, an[illegible] 309. Trans. A. I. M. E., 18, 666. Industries, Vol. V, p. 405.

1892 to March 15, 1895,[1] there has been much pub- egarding the work of M. Henri Moissan, who has done ı fine work in the field of high temperatures, and has ished such wonderful results.

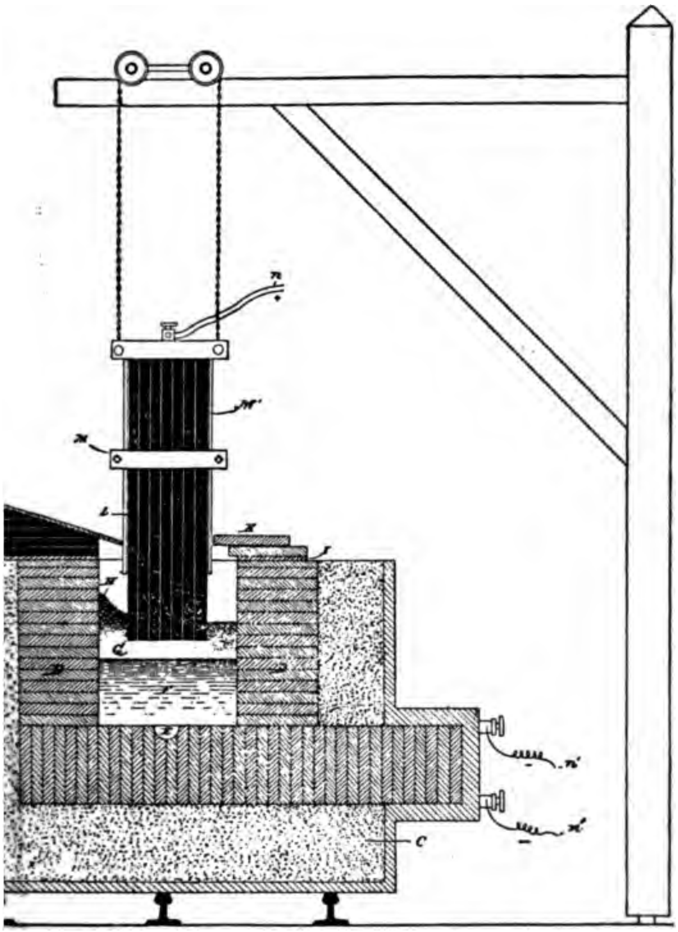


Fig. 8. Heroult's Furnace.

ıployed various styles of furnaces and different amounts nt. His early furnace (Fig. 9) consisted of a simple quicklime suitably bound, and provided with electrodes

. *rend.*, 115, 1031; 116, 549; 117, 679; 118, 116 and 501. La Nature, Vol. 21, pt. 15 and 275. *Ann. Chim. Phys.* [7], 4, 386.

l a cover. In this some very interesting results were obtained.

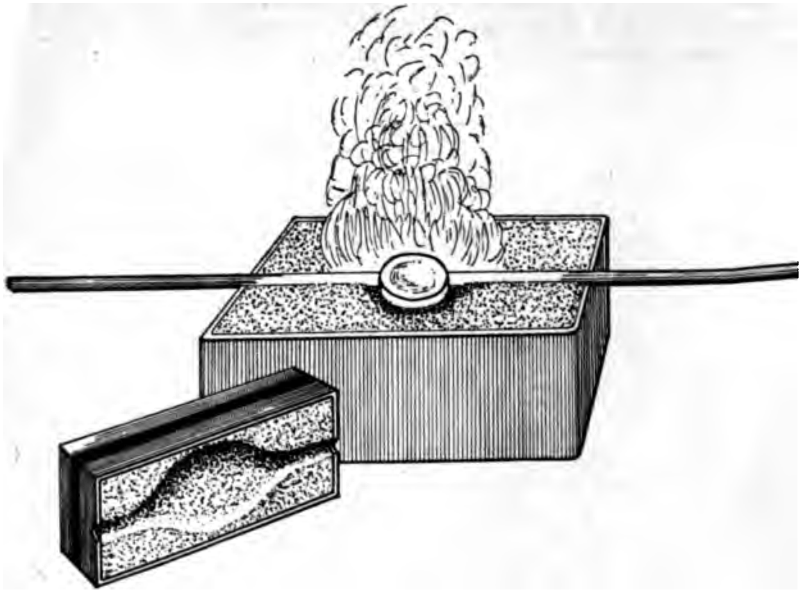


Fig. 9. Moissan's Early Furnace.

Another furnace (Fig. 10) was especially designed for determin the temperature by the specific heat method. A piece of carbon

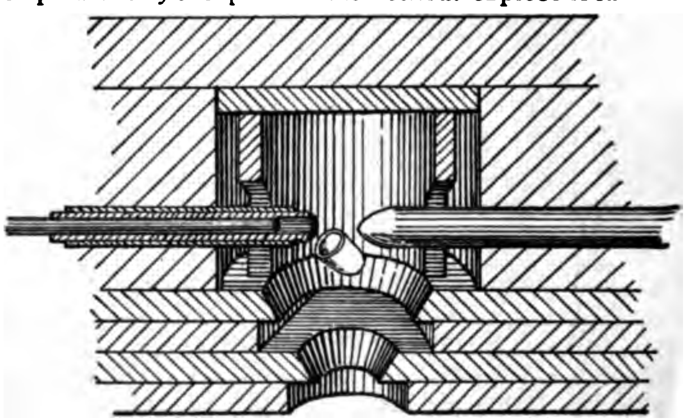


Fig. 10. Mossian's Specific Heat Furnace.

put on the end of one electrode, the current passed, and the bon pushed off from the electrode, at the same time a slid

withdrawn from the bottom of the furnace and the hot carbon allowed to fall in the calorimeter below. A number of temperature determinations were made in connection with M. Violle. Another furnace (Fig. 11) was provided with tubes for the intro-

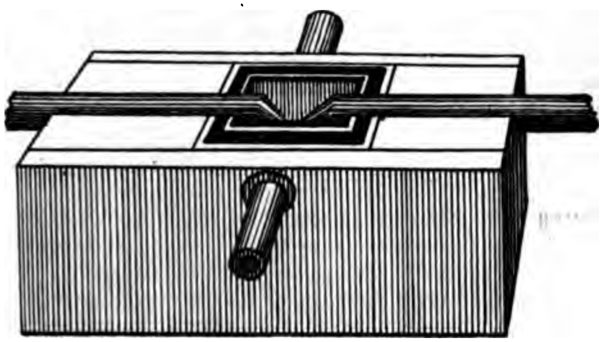


Fig. 11. Moissan's Furnace for Gas Reactions.

duction of gases. In this pure and colorless carbide of silicon was formed from carbon and silicon vapors. This furnace also had various layers, beginning with lime on the outside, and fol-

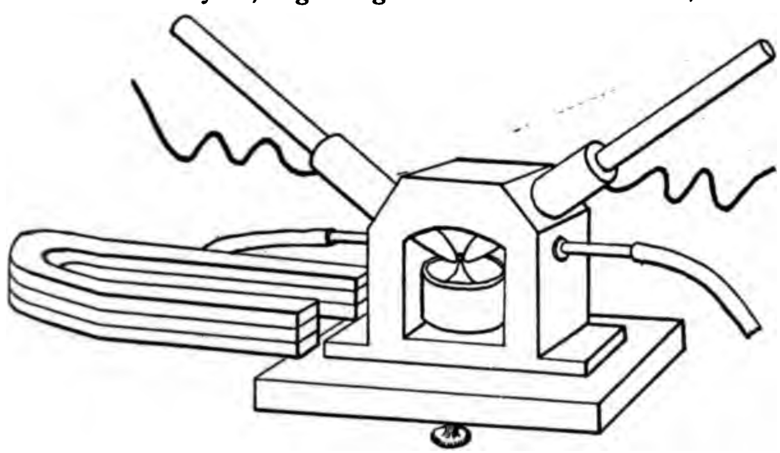


Fig. 12. Moissan's Furnace with Transparent Ends and Magnet.

lowed by carbon and then magnesia on the inside, or vice versa. Another furnace (Fig. 12) had transparent ends of glass, or mica, so that the operations could be watched. It also had magnets to direct and control the arc.

In this work Moissan designed to investigate and study the simple heating effect of the current separated as much as possi-

ble from any electrolytic effect. He speaks of and treats the arc as one would speak of an ordinary flame.

Moissan began with a very moderate current of thirty-five to forty amperes at fifty-five volts, and passed through various stages up to 1200–1600 amperes at 110 volts.

A few of the results obtained by Moissan may be mentioned. Magnesia was the only irreducible oxide found, it was melted and volatilized. Lime, strontia and magnesia began to volatilize before melting. Lime was easily melted and the metal calcium reduced, but it immediately combined with the carbon vapor forming calcium carbide (CaC_2). Alumina and platinum were volatilized. Artificial diamonds were produced. Various temperatures from 2000° to about 3800° C., were measured. Carbon begins to volatilize at about 3500° C. Various quantities of the rarer metals were reduced, 200 to 300 grams of uranium; 100 grams of vanadium; ten kilos of chromium, as well as manganese.

As in practical flame work the amount of fuel burned determines the temperature of the furnace, so in this case the amount of current passed determines the temperature and the furnace must be designed to stand the current to be employed. While Moissan's small furnace will stand the temperature developed by small currents, yet with 1200 amperes at 110 volts the lime and magnesia melts down, volatilize rapidly, and in a few moments the furnace is spoiled at a temperature of about 3500° C.

For materials of construction it was found that lime was the best nonconductor for heat, but its fusibility and the ease of forming the carbide, prevent its use for the inside of the furnace at very high temperatures. Compared with lime, carbon is a good conductor of heat. Magnesia is also a better heat conductor than lime. It does not form carbide of magnesium, and therefore can be heated very hot in direct contact with carbon, while lime cannot. It, however, is volatile, and can be melted at very high temperature. Practically, therefore, the outside of the furnace is quicklime, while the interior is variously lined with carbon or magnesia, or both, and when carbon is in direct contact with the lime it must not get too hot at the point of contact.

In 1893 a United States patent, No. 492,767,[1] was issued to E. G. Acheson, in which a mixture of silica, carbon, and salt was heated by the passage of the current and silicon carbide produced, which has found considerable application as an abrasive.

In the present early stage and activity of the calcium car-

[1] See also *J. Franklin Inst.*, 136, 194 and 229; 137, 401. Sci. Am., 70, 215. West. Elec., 17, 271. N. Y. Sun, Oct. 20, 1895. Cassiers Mag., 9, 387.

bide and barium carbide questions it might not be wise to go into the details of the work and the claims of the various workers (Borscher, Maquenne, Moissan, Travers, Willson, I arrange these names simply alphabetically) but I mention these various carbide processes to show the present condition of our subject, and to draw special attention to a notable fact.

In reviewing our subject we find that in the early days the current was suggested, tried and used for various metallurgical operations, in which both the heating and decomposing actions of the current were utilized. Then in the principal, practical part of the field, that of the production of sodium and aluminum, the generation of intense temperatures became paramount. This activity culminated in the high heat processes of Cowles and Heroult, and they were very soon superseded by the low temperature processes of Hall for the production of aluminum, which carried with it the greater part of the demand for the production of sodium.

At the present day, therefore, there is no practical production of metals by high electric heats, with the possible exception of the production of chromium. On the other hand, high electric heats are being employed to go a step beyond the reduction of the metals, and to form new compounds, as in the carbide processes mentioned. In these the metals are first reduced, and are then immediately recombined with carbon, and thus in the field of high heat our subject becomes the application of high electric heat to chemistry.

Jan. 14, 1896. FREDERIC P. DEWEY.

NOTES.

The Second International Congress of Applied Chemistry.—The First International Congress of Applied Chemistry was held at Brussels, under the patronage of the Belgian Government, from August 4th to 11th, 1894. On the last day of the meeting it was voted to hold the next congress in Paris, in 1896. This approaching congress will be held in August of this year, the exact date to be hereafter published in this Journal, under the patronage of the French Government and pursuant to a plan of organization formulated by the Association of Chemists of the Sugar Industry and Distilling in France and the Colonies. M. Berthelot, the distinguished chemist, and now Minister of Foreign Affairs, is one of the Presidents of Honor. The congress will be held in ten sections, as follows:

Sec. I. Chemistry applied to the sugar industry.

Sec. II. Fermented and distilled beverages, cider, and vinegar.

Sec. III. Agricultural industries, including dairying, starch making, bread making, milling, etc.

Sec. IV. Agricultural chemistry, including fertilizers, soils, waters, cattle feeding, etc.

Sec. V. Chemistry applied to the customs, including methods of analysis of all the dutiable substances where the duty depends on chemical composition.

Sec. VI. Fats, tannin, rubber, paints, color, paper, etc.

Sec. VII. Photography.

Sec. VIII. Metallurgy.

Sec. IX. Biochemistry, foods, poisons, potable waters, microscopy, bacteriology, spectroscopy, etc.

Sec. X. Electrochemistry.

The undersigned committee for the United States has been appointed by the Provisional Council of the Congress, and we beg to call the attention of all American chemists, who expect to visit Europe during the coming summer, to the desirability of attending the meetings of the Congress. On application, the chairman of the committee will send a copy of the provisional program, showing the character of the questions which will be under discussion and containing a blank application for membership, which should be filled and sent to the proper address, before the date of the meeting. Already more than 900 chemists have entered their names as members of the Congress, and it is confidently expected that the membership will reach 2000. The committee respectfully invites the cooperation of all American chemists who hope to be able to attend the meetings or contribute papers for discussion.

Dr. H. W. Wiley, Dept. of Agriculture, Washington, D. C., Chairman.

Prof. Peter T. Austen, Polytechnic Institute, Brooklyn, N. Y.

Prof. F. W. Clarke, U. S. Geological Survey, Washington, D. C.

Dr. Charles B. Dudley, Pres. Amer. Chem. Society, Altoona, Pa.

Prof. F. A. Gooch, Yale University, New Haven, Conn.

Prof. Charles Loring Jackson, Harvard Univ., Cambridge, Mass.

Dr. Wm. McMurtrie, 106 Wall St., N. Y. City.

Prof. Charles E. Munroe, Columbian Univ. Washington, D.C.

Prof. Albert B. Prescott, Univ. of Michigan, Ann Arbor, Mich.

Prof. W. B. Rising, Univ. of Cal., Berkeley, Cal.

Dr. G. L. Spencer, Centralia, Wis.

Dr. W. C. Stubbs, Audubon Park, New Orleans, La.

Dr. Thomas Taylor, Washington, D. C.

The Cyanide Method of Extracting Gold from its Ores. Application to the Assays of Ores Poor in Gold and Silver.[1]—*Preliminary Notice.*—Having undertaken this work, at the suggestion of Prof. Mallet, only within the last two or three weeks, I have no exhaustive report of any nature to present. The work has not, as yet, advanced to such a stage that results can be stated satisfactorily in numbers. The attempts to apply this method to assay purposes *may* have been already made. If so, I have been unable to find any statement of that fact, and have no knowledge that such an attempt has been made.

I am at present comparing the method with the methods using chlorine and bromine. Quartz ores, too poor in gold or silver to be advantageously worked by the ordinary method of crucible assay, are the ores so far used.

The pulverized ore is well and repeatedly shaken with 0.25 per cent. solution of potassium cyanide, free access of air being provided for. After filtration and partial evaporation, the liquid is slowly passed over pure zinc filings. The zinc is then scorified with a larger amount of lead and the button cupelled.

The work has only progressed far enough to give hopes of good results. It seems at this stage to offer several advantages over the other methods mentioned.

The cyanide extracts the silver as well as the gold; bromine and chlorine only extracting the gold. The extremely disagreeable fumes of the other methods are entirely avoided. The work can be conducted without the use of hoods of fume rooms.

[1] Read at the Cleveland meeting, December 31, 1895.

The method yields the metals in a condition in which they ca be more easily handled and their weights determined than ca be the exceedingly fine precipitate from the bromine or chlorin solution.

The time is materially shortened, the long delay in the collec tion of the gold by the use of ferrous sulphate or oxalic aci being avoided.

In the few comparisons made, the amount of gold (and silver extracted has been greater with the cyanide method than wit the others. Though sufficient work has not as yet been done t make this reliable.

Before pronouncing on the availability of the method, othe classes of ores than those so far used (quartz ore with and wit out pyrite) will be treated.

I expect to push the work as rapidly as possible.

Jan. 3, 1896. WILLIAM J. MARTIN, JR.

BOOKS RECEIVED.

Mining Journal of the Northwestern Mining Association. Spoka ne, Wash. 58 pp. Price 10 cents.

A Text-Book of Gas Manufacture for Students. By John Hornby, F. C. New York: Macmillan & Co., 1896. xiv + 216 pp. Price $1.50.

Bulletin No. 59. Spraying Experiments in 1895. Lexington, y.: Kentucky Agricultural Experiment Station of the State College of en-tucky. December, 1895. 19 pp.

Bulletin No. 60. Analyses of Commercial Fertilizers. I. Official al-yses. II. Analyses of Farmers' and Inspectors' Samples. Lexing on, Ky: Kentucky Agricultural Experiment Station of the State College of Kentucky. December, 1895. 12 pp.

VOL. XVIII. [APRIL, 1896.] No. 4.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE MANUFACTURE OF CALCIUM CARBIDE.[1]

BY J. T. MOREHEAD AND G. DE CHALMOT.

Received January 27, 1895.

SO universal is the interest in acetylene gas and so different the estimates and opinions as to the cost of calcium carbide as a source of the cheap production of acetylene gas, that we have thought it desirable to place on record the data from our actual experience in the production of calcium carbide in quantities. The works of the Willson Aluminum Company have been running night and day since May 1st, 1895, producing calcium carbide. These works are daily duplicating the results here given and can expand indefinitely. Each individual step, except water power, as taken at Spray, N. C., is capable of being changed in the direction of reducing the cost of the output, as these efforts have been attended with the clumsiness, lack of adaptability and excessive cost that is incident to all efforts along an untrodden path. Still we can produce calcium carbide at less than $25.00 per ton, including wear and tear and interest on capital.

Beyond looking after the dynamos, no special training is necessary, as neither metallurgical nor chemical skill is required in the operations. We grind and mix coke and lime, start the water wheel, see that the arc is formed, shovel in the mixture of lime and coke and the volt- and ammeter show when to lower or

[1] Read Sept. 3d, before the Springfield meeting of the A. A. A. S. by one of us (M). We have made since then several additions, so as to make the article complete up to the present time.

raise the carbon pencils, which is done by means of a screw located in the dynamo room, away from the furnace. We can measure with an ordinary yard stick on this screw the height of the piece of carbide in the furnace. We stop when we have raised the carbon pencils thirty-three inches, switch the current off to another furnace and repeat the operation. The carbide in the former furnace, as soon as cooled and brought in contact with water, is all ready to do perfect work in generating acetylene gas; it will proceed with this work without help and will make room therefor in spite even of bands of steel.

Water power costs us $6.00 per horse power. Water in the raceways ready for the water wheels is now offered in enormous quantities to the Willson Aluminum Company at the rate of $5.00 per horse power per year. These powers are located at different places, where coke and lime can be had cheaply, and also cheap transportation for the carbide to the market.

The technical description of our process which follows herewith was written by G. de Chalmot, who has had for some time personal supervision of the operations of the Willson Aluminum Company.

In the year 1888 Mr. T. L. Willson started a series of experiments with a view of reducing refractory ores in the electric furnace, and among other valuable things he made calcium carbide.[1]

We will first give a short description of the furnace and a general outline of the process, then enlarge somewhat on the details. The furnace used in Spray, N. C., is built of ordinary brick (a sectional front view is given in figure 1). The front side is formed by four iron doors, the one above the other. The upper two remain closed usually. The chimney is attached near the top of the furnace, and commences with a flue m in the corner. The furnace measures at the bottom inside two and one-half by three feet. The electric current enters at the bottom,

[1] We will note here that Moissan, who discovered this process for making carbide independently of Mr. Willson, communicated incidentally at the meeting of the French Academy of December 12th, 1892, (*Compt. Rend.*, 115, 1033) that a carbide of calcium is formed if calcium oxide is heated in an electric furnace with carbon electrodes. He investigated the compound much later (*Compt. Rend.*, 118, 50). Mr. Willson, who sent during the summer of 1892 samples of carbide for examination to Lord Kelvin, of the Glasgow University, clearly antedates Moissan. See Journal of Franklin Institute, 1895, page 333.—Note.

and top. The bottom electrode is an iron plate a covered with eight inches of carbon b. For this covering we use pieces of

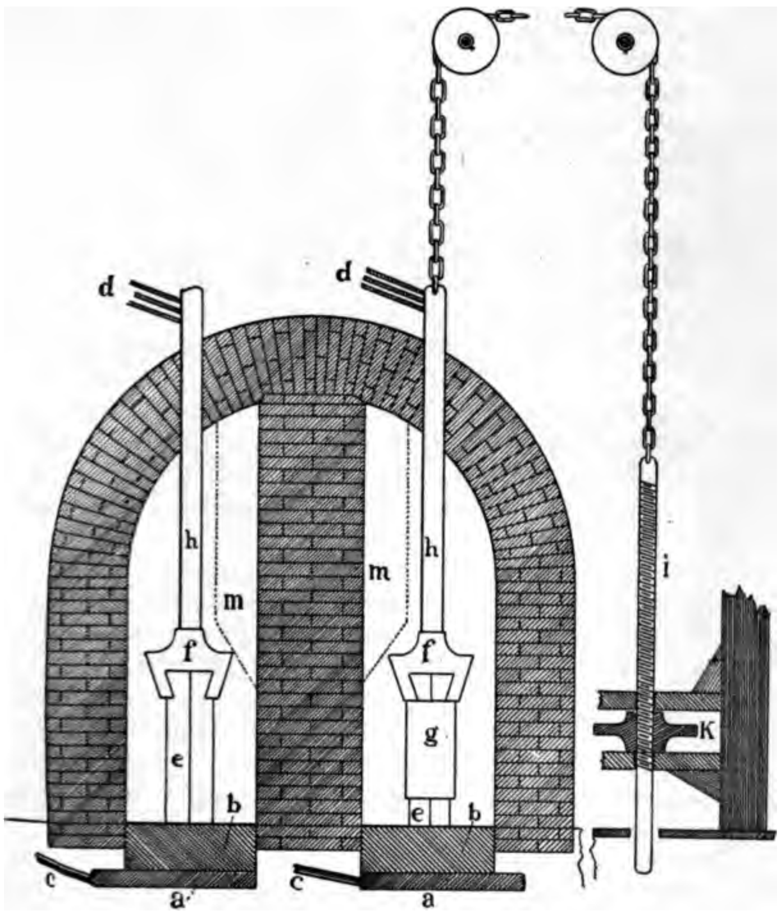


Fig 1.

carbon pencils or a mixture of coke and coal tar. Sixteen copper cables of 0.75 inch in diameter c convey the electricity from the dynamos to the bottom electrode.

Sixteen other cables are connected with the top electrode d. The top electrode is composed of six carbon pencils e, each four inches square and thirty-six inches long. Six pencils are

arranged in three pairs behind each other and are cut out at the top so as to fit in the carbon holder f. They are enveloped together by a sheet of iron g, which is shown in the right-handed furnace of figure 1. They really form one pencil. The carbon holder is screwed to a copper bar h, which is three inches square and to which the copper cables are connected. This bar is fastened by a chain that runs over two pulleys to a long upright screw i. On this screw is a nut which forms the center of a wheel k. By turning the wheel the screw can be raised or lowered. The man who attends to the wheel has the volt- and ammeter before him. The electric current is generated in two dynamos to which transformers are connected, and which can give a current of from fifty to 100 volts. The power is furnished by a water wheel of 300 horse power under twenty-eight feet fall.

Two of the furnaces have been working for twelve months and they have given satisfaction, except for working not sufficiently economically. In the furnaces built for the Niagara Falls Carbide plant, many changes which we suggested, have been adopted, looking to economy of production. We give here a short description of these furnaces (figures 2 and 3).

In Spray it is necessary to allow the furnace to cool before emptying it. In order to use one and the same furnace continuously, the bottom of the furnace is replaced by an iron car a which runs on a track and in which carbide is formed. When the car is filled the pencils b have been lifted entirely out of it. The current is then shut off, door c is opened, the full car is run out and replaced by an empty car. The pencils are lowered again to the bottom of the car and a new run is commenced.

The bottom of the car is covered with from four to eight inches of carbon. When the contents of the car have sufficiently cooled outside the furnace, which will take from six to twelve hours, the body of the car is lifted from the track by the trunnions d and turned over. The contents are dropped on a grate formed of iron bars, on which the piece of carbide remains, while the unreduced material falls through into a lower room where it is collected to be used again for the formation of carbide. The mixture of lime and coke is fed into the car through the flues e.

ɛtend along the whole length of the car. The rods f
:ar four blades, extend through the whole breadth of

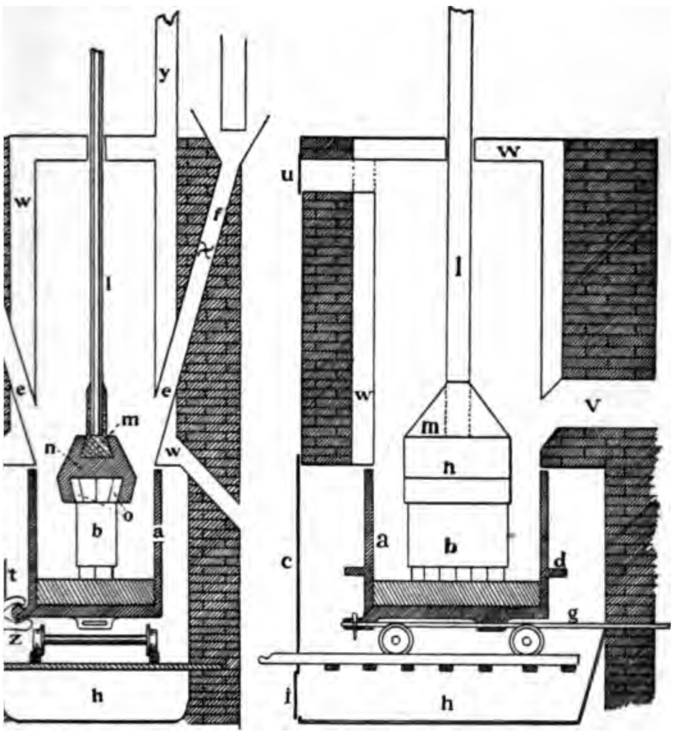


Fig. 2. Fig. 3.

ng flues. These rods are turned automatically, and r they turn, the more material is fed into the car. In stoke the furnace automatically, the car is attached to ɔar g by two hangers and a coupling in front of the car. ɛtends through the back wall of the furnace, and is cally moved forward and backward for about two inches ıt twenty times per minute. The car is thus also rolled d and forward on the track for about two inches each ;very time that the car stops or starts it gets a little jerk sufficient to fill up the holes made by the escaping the loose material. This motion of the car further the arc being located for a longer time at one point, for

which the arc has always a great tendency. This will materia[illegible] increase the efficient use of the heat of the arc. Under the tra[illegible] of the car is the bin h in which the unreduced material is c[illegible] lected that will fall from the car when this is taken out. T[illegible] material can from time to time be taken out through the doo[illegible] The carbon holder is more complicated than in the Spray f[illegible] nace. Twelve carbons are used and the holder is theref[illegible] about twice as heavy. It is not advisable to suspend this c[illegible] bon holder from a copper bar, which moreover becomes rat[illegible] hot in this closed furnace. The carbon holder is theref[illegible] attached to a rod l, which is composed of three slabs. T[illegible] inner one is of copper and measures six by one and one-h[illegible] inches, and the outer ones are of iron and are six inches by o[illegible] Since it is not practical to attach the twelve carbons in th[illegible] iron casings to the carbon holder in the furnace, the holder its[illegible] is composed of two pieces, m and n, which slide into each oth[illegible] The aggregate of pencils is connected to piece n outside t[illegible] furnace and the whole is placed in the car a. Rod l is so [illegible] lowered that piece m will easily slide into piece n, and the co[illegible] nection can easily be effected. Iron plates o are placed betwe[illegible] the carbon holder proper and the pencils. These plates o a[illegible] about one inch thick. They are fastened to the inside of t[illegible] carbon holder by pins which are inserted in the holder, and [illegible] in holes of the plates. These plates can be easily r[illegible] moved and replaced. It will sometimes happen that small arc is started between the pencils and the inside [illegible] the carbon holder and a part of the carbon holder will melt. I[illegible] the case that the plates o are used, one can simply replace the[illegible] plates. The car a forms one of the electrodes and is connecte[illegible] with the bottom cables q by two clamps p. The lower clamp stationary and the upper one can be opened. The clamps a[illegible] tightened around the appendage z of the car by a wedge a[illegible] screw s. When the clamps are fastened the slide t is lowered [illegible] as to shut the opening. The electric connection with the c[illegible] can also be and is better made through the bar g, which in th[illegible] case is composed of an iron and copper slab. It may also [illegible] made by two copper bars which run alongside of the car and a[illegible] pressed against it with springs. The furnace is entirely close[illegible]

When it is started the door c is shut, but the door u is kept open till the carbon monoxide, which is formed in the reaction, has replaced the air in the furnace. This point is reached when the flame comes out of this door. Door u is then also closed and the gases escape through the chimney v. The use of door u prevents explosions of the carbon monoxide in the closed furnace. Chimney v begins just over the car. The carbon holder and the rod l are therefore not in the current of the hot gases. The upper part of the furnace is cooled moreover by an air jacket w through which a draught of air is maintained. The cold air enters through openings x and the warm air is led off by chimney y. The warm air may be utilized for heating the building. The chimney gases pass through flues or rooms, in which the lime dust is collected by proper means. Owing to valuable suggestions of our superintendent, Mr. J. C. King, this furnace is called the King furnace. Besides these two types of furnaces, several others have been proposed.

In order to start our present furnace, we shut the lower iron door and lower the pencils to the bottom of the furnace. The current is turned on and the mixture of coke and lime fed in, the arc being kept covered with the mixture as high as one foot around the pencils. It is then easier to keep the arc steady. It is necessary to stoke from time to time, for the gases which are formed in the arc constantly make channels through the material, and especially if unslacked lime is used. These channels will not fall in and less material will come into the arc. The feeding in of the material is continued for several hours. If the attendant at the hand wheel sees that the voltage becomes low, he raises the pencils. If the arc should be broken the amperage becomes zero and the voltage high, and in that case the pencils are quickly lowered. After shutting off the current it is well to allow the furnace to cool two or three hours before emptying it.

The carbide is always found in one piece between the pencils and the bottom. It has a conical form, being broader at the base and can be two and one-half feet high in our furnace. It however never has so great a diameter as to fill up the whole capacity of the furnace. The carbide is therefore entirely sur-

rounded by a cover of the mixture of lime and coke. This mixture is so bad a conductor of heat that the brick walls of the furnace are not attacked. It is very easy to separate the carbide from the loose mixture, for the latter never melts, together, while the carbide is hard and solid. The pieces of carbide are covered with a thin coating which is a little thicker at the top of the piece, and the same may be reground and again used. This coating contains mainly carbon, but also carbide and calcium oxide. It seldom yields more than a half cubic foot of gas per pound, but in some cases it yields 1.77 and even 2.10 cubic feet. This coating, however, is of little importance. If the mixture is well made this coating seldom exceeds from twenty to thirty pounds on a piece of carbide of from 300 to 400 pounds. The carbide itself is crystalline. The crystals are especially well developed near the top and are more perfect with an excess of coke, low voltage and when allowed to cool slowly. The center of the piece of carbide stays liquid for some time after the electric current has been shut off. The liquid part, however, is of the same quality as the rest of the piece. We have in fact tapped out of the furnace, carbide which was very pure and yielded 5.59 cubic feet of gas per pound. We do not wish to express an opinion as to the practicability of tapping the carbide as soon as it is formed. We will only mention that Mr. Price, in Newark, has, with a view of tapping the carbide, constructed and patented a new furnace, and that one of us (C.) has also devised a furnace for the same purpose.

Carbide of average quality (about five cubic feet of gas per pound) often has a reddish color, especially if it has been made with a current of high voltage. Carbide of bad quality is often grayish or blackish, or will show streaks of graphite. Pure carbide yields more than 5.90 cubic feet of gas per pound. It has, however, been found to be more economical to produce carbide that yields only about five cubic feet of gas per pound. Samples of carbide of different qualities contained:

TABLE I.

Cubic feet gas per pound.	Carbide. Per cent.	Free calcium oxide. Per cent.	Carbon. Per cent.	Other impurities. Per cent.
5.7	96.6	0.6	....	2.8
5.5	93.2	4.2	....	2.6
5.1	86.4	9.5	....	4.1
5.025	84.7	10.7	1.6	3.0
3.6	61.0	27.5	3.2	8.3
3.45	58.5	1.1	25.6	14.8

The upper part of a piece of carbide is often purer than the under part.

The coke to be used should not contain much ash. Our coke contains about seven per cent. of ash. The carbide obtained with a coke of from ten to eleven per cent. of ash was perceptibly inferior to that obtained with our usual coke. It was found impracticable to make a good quality of carbide with a coke of twenty-seven per cent. ash. It is well that there should not be more than ten per cent. of ash in the coke. The coke should be ground very fine, and it should pass through a fifty mesh sieve. The lime need not be as fine as the coke. The largest pieces should pass through a ten mesh sieve. If the lime is coarser the quality of the carbide becomes inferior. That the state of the pulverization of the lime is important, can be seen by a comparison of the average amount of gas per pound (4.97 cubic feet), obtained with unslaked lime (Table II), and that obtained with air-slaked lime (5.27 cubic feet Table III). The unslaked lime was in several instances not quite as fine as the slaked lime. Unslaked lime is decidedly preferable to air-slaked lime, as we will see afterwards.

The lime which we use contains one and one-half per cent. magnesia and one per cent. of the other impurities. The anhydrous lime should contain ninety-five per cent. calcium oxide, and no more than five per cent. impurities. The presence of magnesia is especially detrimental to the production of carbide. We could not obtain a good quality of carbide with a lime in the following analysis: Insoluble, 0.24 per cent.; silica, 0.78 per cent.; ferric oxide and alumina, 0.68 per cent.; calcium oxide, 92.83 per cent.; magnesium oxide, 5.47 per cent. Further experiments showed that two and one-half per cent. of magnesia in

the mixture has a marked influence on the production. Th lime used for making carbide should not contain over three pe cent. of magnesia. That magnesia has such a bad influenc upon the formation of carbide is probably due to its forming veil between the carbon and the lime particles preventing the combination. Magnesia does not unite either with lime or wi carbon. The latter fact was first shown by Moissan,[1] and o own experiments in this line fully confirm his results. The li and the coke must be mixed very well or the carbide will be inferior quality and there will be much coating. Besides t carbide some mixture remains in the furnace. More carb than lime burns out or volatilizes in an open furnace. It therefore necessary to add carbon to this mixture before using again. The amount to be added is calculated from the result an analysis of the mixture. If coke is added in the proper pr portions, the unsmelted portion of the material can be returne at least three times into the furnace, and still yield good carbid The impurities of the lime and the coke ashes remain as well i the carbide as in the residual mixture. It is therefore a goo practice to add charcoal instead of coke to the mixture, so a not perceptibly to increase the amount of ash. The mixtu that comes from the furnace is red hot and it will stay hot fo days. It will lose a large amount of carbon if allowed to lay i heaps in the air. It is better to mix in the necessary amounts o carbon and use the mixture at once again. One can also kee the mixture in air-tight sheet-iron tanks. If the lime has bee unslaked the mixture cools much quicker and does not lose a much carbon after it has been taken from the furnace. In th case of slaked lime, water gas is probably formed in larg amounts. The carbon pencils must be well cared for in orde that they last for a long time. If sufficient coke is put in th mixture they are not attacked much at the end. They wi shorten from 0.05 to 0.10 inch for every hour running. The become thinner for being exposed to the air when hot. The are mainly attacked after the electric current has been shut off for if the furnace is working the gases from the arc come u around the carbons and shut the air off. In order to save th

[1] *Compt. rend.*, 118, 506.

carbons best it is therefore well to keep the furnaces running with as little interruption as possible. In the closed furnace, which we have described, the carbons will be surrounded by non-oxidizing gases, which will save them materially. In the open furnaces in Spray we surround the carbons with a sheet iron cover that reaches from the carbon holder to within four inches of the bottom end of the carbons. This jacket is fastened with iron wires to the carbon holder. The space between the carbons and the jacket is packed with a mixture of coke and coal tar or pitch. This mixture is baked by surrounding the carbons and jacket with the red hot material that comes from the furnace or by placing them in a fire. The jacket will generally last as long as the carbons. One set of the carbons in an open furnace and with interrupted operations will last on an average about 100 hours. These figures hold good where a current of from 1,700 to 2,000 amperes is used. The voltage has no perceptible influence on the result. Working with say 1,700 amperes and 100 volts and generating about 225 horse power, the production of carbide per hour can be reckoned to be easily eighty-five pounds, and one set of carbons can therefore make at least 8,500 pounds of carbide, even in an open furnace. If the furnace is used continuously the carbons will last at least from 200 to 300 hours, and the cost of pencils for one ton of carbide will be about $1.00.

The analytical part of our work has been very simple. After the piece of carbide has been broken open with a hammer, two or more samples, representing as nearly as possible the average quality of the carbide and of about eight ounces each, are taken. These samples are broken in pieces of about one-half inch in diameter and from two to three ounces are taken for one gas test. The material is put into a dry bottle of about one quart capacity, which is provided with a rubber stopper, through which two glass tubes pass. The one tube bears a stop-cock and drop funnel, the other tube conducts the gas through a series of U-tubes and then through a small gas-meter. The funnel is filled with water, and by opening the stop-cock, water is allowed to drop slowly on the carbide. The acetylene gas is generated and is cooled in the U-tubes before it passes to the

gas-meter. Much water vapor is condensed in the U-tubes, for the gases generated in the bottle are hot. We make a correction for the temperature of the gas as it passes the gas-meter. We do not take into consideration the small amount of gas which passes through the gas-meter by the expansion of the gas in the bottle when the latter becomes hot, and because a part of the bottle becomes filled with water. The error arising herefrom is of no consequence, for the volume of the bottle is only one quart and the volume of the gas which passes from the gas-meter is from one-half to one cubic foot. The water, moreover, becomes saturated with acetylene. Our figures show the amount of moist gas at the temperatures of 60° F.

In order to determine the lime in the mixture, two and five-tenths grams are boiled with a slight excess of hydrochloric acid of known strength in a 250 cc. bottle. The bottle is cooled and filled up. The liquid is filtered and in fifty cc. of the filtrate the excess of acid is determined by titration. The coke is determined by boiling two grams of mixture with twenty-five cc. of twelve per cent. hydrochloric acid and filtering off the coke on a Gooch crucible. These methods do not make a claim to absolute accuracy, but they can be quickly executed and give a good estimate of the relation in which the coke and lime are present in the mixture, as the following figures show. The coke used for the original mixture contained 7.33 per cent. of ash. The coke that remained from the mixture that had been boiled with twelve per cent. hydrochloric acid contained six and eight-tenths per cent. of ash, and the coke which remained by the same treatment from a similar mixture that had been once in the furnace contained seven and eight-tenths per cent. ash. The amount of lime found in mixtures by titration and that found by gravimetric analysis varied only by from one-half to three-quarters per cent. when the small amount of magnesia in the lime was known and taken into consideration. In controlling the different runs we have proceeded as follows:

The carbide was weighed and the coating on it determined either by takng it off and weighing it or by estimating it on small and clean pieces. By deducting the weight of the coating from the weight of the piece of carbide we obtain the net yield

of carbide. The gas therein is determined, the figure accepted being the average of the result of the analyses of at least two samples. In order to determine the power used, we multiply the voltage by the amperage and divide the product by 746 to obtain the number of horse power generated by the dynamos. In order to make a more proper comparison we found it necessary to deduct the loss of voltage sustained in the carbon pencils. Our pencils were made in different factories and had a different resistance. We therefore determined the difference in voltage as indicated by the usual reading of our meter and the voltage at the end of the carbon pencils. We touch the end of each pencil alternately with an iron rod that is connected with the volt-meter by a copper wire. We call net power the power generated by the dynamos less the average loss in the six carbon pencils. Our meters are placed in the primary circuit and we have not taken into account the losses of amperage in the transformers and those sustained by leakage. We have further found that the readings of our meters are about six per cent. higher than those of standard Weston meters. It may therefore be safely relied upon that all our estimates for the production of carbide per horse power are too low. The error is, however, in all cases in the same direction, so that it cannot have materially influenced our deductions, which are based upon a comparison of our results.

In the carbide there is also a considerable loss of voltage and therefore of power. We found, for example, sixty-five volts in the bottom cables and only fifty volts at the top of a two and a half feet high piece of carbide just under the arc. This makes a loss of six volts for each one foot of carbide. The average production during six to eight hours of continuous working is as large as that during two or three hours at the same power. It is, however, not advisable to make the carbide pieces higher than two and a half feet, since then the resistance of the carbide will begin to materially reduce the quantity of the production.

Taking into account the weight of the product, the time in which it has been produced and the number of horse power used, we calculate for each run the amount of pounds produced per horse

power in twenty-four hours. By multiplying these figures by the number of cubic feet of gas produced per pound we obtained the number of cubic feet of gas produced per horse power in twenty-four hours. In the following table we give the results of experiments wherein everything has been determined, wherein both unslaked and slaked lime have been used and voltage, amperage, and duration of runs were varied. Since these results were obtained we have had many visitors from all parts of the country and for each party we have made a test run. The result of these runs have all confirmed our previous results, with on exception, which was due to the presence of five and a half per cent. magnesia in the lime.

TABLE II. UNSLAKED LIME.

Date.	Time of experiment. Hours.	Volts.	Amperes.	Loss of voltage in the pencils. Per cent.	Horse power.	Production in twenty-four hours including slag. Pounds.	Net production. Pounds.	Cubic feet of gas per hour.	Cubic feet of gas per horse power in twenty-four hours.
June 27th	2.50	100	1700	7.0	214	9.87	9.42	4.83	45.50
July 2nd	3.00	100	1666	8.0	205	10.34	9.76	5.25	51.24
" 1st	2.25	100	1700	10.0	205	10.66	10.10	4.66	47.06
June 24th	3.20	100	1600	7.0	214	11.50	10.73	4.93	52.90
" 28th	2.50	100	1700	10.0	205	11.70	11.10	4.75	52.72
July 18th	3.00	65	2000	5.0	165	9.63	9.15	4.95	45.29
" 19th	3.00	65	1900	5.0	158	10.40	9.62	4.83	46.46
" 5th	3.75	65	2000	5.0	165	8.38	8.15	5.40	44.01
" 9th	4.50	65	2000	5.0	165	9.50	9.05	4.99	45.16
Aug. 10th	6.00	65	1800	8.0	144	9.34	9.00	5.39	48.51
" 13th	6.00	65	1800	8.0	144	10.83	10.44	4.82	50.32
July 31st	7.00	75	1800	8.5	166	11.44	10.53	4.83	50.[illegible]6
					Average,		9.75	4.97	48.[illegible]3

TABLE III. AIR-SLAKED LIME.

Date.		Time of experiment. Hours	Volts.	Amperes.	Loss of voltage in the pencils. Per cent.	Horse power.	Production per horse power in twenty-four hours, including slag. Pounds.	Net production. Pounds.	Cubic feet of gas per pound.	Cubic feet of gas per horse power in twenty-four hours.
June	25th	5.00	100	1700	7.0	214	8.34	7.96	5.30	42.19
"	29th	4.00	100	1700	10.0	205	8.78	8.34	4.98	41.53
"	19th	5.50	100	1700	7.0	214	9.25	....	4.89	....
"	22nd	4.00	100	1600	7.0	199	9.80	9.65	4.74	45.75
Aug.	14th	4.50	75	1700	7.0	159	7.88	7.13	5.50	39.22
July	12th	3.75	85	1800	3.5	198	...	6.33	5.55	35.13
"	26th	8.00	75	1800	5.0	172	8.40	7.23	5.33	38.54
"	12th	5.50	85	1775	8.0	185	...	7.32	5.32	38.94
"	6th	5.00	80	1020	3.0	200	8.78	8.16	5.11	41.70
"	23rd	3.00	65	1800	5.0	150	6.83	6.40	5.78	56.99
"	22nd	2.00	65	1800	5.0	150	7.13	6.40	5.62	35.97
"	22nd	2.00	65	1800	5.0	150	7.20	6.40	5.64	36.09
"	25th	9.00	65	1800	5.0	150	7.72	7.27	5.54	40.28
"	20th	4.00	65	1800	5.0	150	8.60	8.00	5.01	40.08
"	23rd	5.00	65	1800	5.0	150	9.02	8.00	5.07	40.56
"	24th	8.00	65	1800	5.0	150	9.30	8.03	4.97	39.91
						Average,		7.51	5.27	39.52

It is obvious that the results obtained from unslaked lime are far better than those with air-slaked lime. This is undoubtedly due to a loss of power used in decomposing the hydrated lime. The unslaked lime used by us contained, after being ground, from five to nine per cent. of water. In practice it is necessary to use the mixture that comes from the furnace again. This mixture always contains some carbonate of lime, but if it be mixed when still hot with the necessary amount of carbon and put again into the furnace the lime has no opportunity to slake. The unslaked lime has the further advantage that it weighs less and is much less bulky, and that the mixtures made from it cool much faster than those made from slaked lime. The only disadvantages of unslacked lime are, that it must be ground and that mixtures made from it require more stoking if put into the furnace. The mixtures of unslaked lime can stand up against the sides of the furnace under a very steep incline and they can leave a hole all around the pencils. The mixture to be used should, on an average, contain 100 parts of

lime and sixty-four to sixty-five parts of carbon in order to obtain a carbide of about five cubic feet of gas per pound. If the voltage is increased to 100 it is better to take a little more carbon (100 lime and sixty-six to sixty-seven carbon). If the voltage is sixty-five or less, sixty-three to sixty-four parts of carbon are sufficient. If the amount of carbon is increased the carbide becomes purer, but there is often more coating.

The largest amount of gas per horse power is obtained if the carbide yields about five cubic feet of gas per pound. The yield of carbide in pounds varies inversely with the quality. In the following table we give the results of a series of experiments made with slaked lime and with a current of sixty-five volts and from 1,700 to 2,000 amperes. Several of these experiments have not been taken up in Table II, because the amount of slag on all the pieces of carbide has not been determined.

Date.	Production per horse power including slag. Pounds.	Cubic feet gas per pound.
July 23rd	6.85	5.78
June 14th	7.10	5.80
July 22nd	7.13	5.62
" 22nd	7.20	5.64
" 25th	7.72	5.54
Aug. 14th	7.88	5.50
May 21st	8.10	5.20
" 22nd	8.30	5.10
July 26th	8.40	5.33
June 4th	8.46	5.52
July 20th	8.60	5.01
June 5th	8.76	4.94
May 28th	8.80	5.20
" 23rd	8.82	5.10
July 23rd	9.02	5.07
June 8th	9.06	5.10
" 24th	9.30	4.97
July 11th	9.30	4.33
Aug. 12th	9.44	4.51
May 31st	9.87	4.30
Aug. 8th	10.52	4.23

Carbide has been made successfully in Spray by the use of both the direct and the alternating current. We cannot express

ɔpinion as to what current can be used to the best advantage, we are not able to compare results. All the results comɑicated in this paper have been obtained by the use of the rnating current. That electrolysis plays a part in the care manufacturing process of Mr. Willson is therefore out of question, and we do not need to use a furnace of the Moisconstruction to prove this. It is not desirable to increase amperage over 2,000 if only six carbons of four inches square used. The higher the amperage the greater the loss of voltin the pencils and therewith that of power. The carbons also last longer if the amperage is low, because they do not ome so hot. Lastly we did not obtain as great a yield per se power if the amperage was high and the voltage corresdingly low. We obtained the best yield of gas per horse er by using a current of 100 volts, which can be seen by ıparing the average of the results in Table II.

TABLE V.

	Volts.	Horse power.	No. of experiment.	Average cubic feet of gas per horse power in twenty-four hours.
Unslaked lime	100	205–214	5	49.88
	65–75	144–165	7	47.23
Slaked lime	100	200–214	3	43.15
	75–85	159–100	5	38.71
	65	150	7	38.55

must be taken into account that we measured the primary ent and that the losses of amperage in the transformers ɔably have been higher when we did not use the highest age, *i. e.*, 100. We do not know in how far it would be adble to increase the voltage over 100, since our dynamos cangive us a current of more than 100 volts. We believe, how-, that the heaty ielded by an arc of 100 volts and from 1,700 000 amperes is about the largest amount to be profitably used he production of carbide in one furnace with six pencils, as used in Spray. We base our assumption on the followfacts: The quality of the carbide becomes better if the voltdecreases. We experienced some trouble in obtaining e carbide crystals with an arc of 100 volts and 1,700 amperes, in order to obtain a carbide that yields more than five cubic

feet of gas per pound the mixture should contain an excess of carbon. If a current of 100 volts and 1,700 amperes is used the furnace requires more attendance and stoking than if a lower power and especially a lower voltage is used. The higher the voltage the faster the pencils must be raised, for if the voltage is low (fifty or sixty-five) the carbide spreads out much more than if the voltage is high (100 volts). In the latter case the carbide builds up as a long thin piece and it is oftener necessary to empty the furnace. As to the time that one furnace should be used continuously, we wish to say that we did not perceive a difference in the quantity and quality of the product whether we ran three hours or from three to nine hours. We must, however, remark that in the case where we used 100 volts and 1,700 amperes with mixtures of unslacked lime we could not continue running for much more than three hours because the construction of the furnace did not admit of raising the pencils quite three feet. With slaked lime we made also with this high power very satisfactory runs of five and five and a half hours. During the first hour the production is somewhat lower. It seems that more heat is lost probably for heating up the furnace.

The mixture used in all of the following experiments contained lime, 50.08 per cent., and coke,[1] 39.22 per cent. The current was of sixty-five volts and 1,800 amperes, the loss of voltage in the pencils five per cent. and the net horse power 150.

TABLE VI.

Time of experiment. hours.	Production per hour in pounds.	Cubic feet of gas per pound.	Cubic feet of gas per hour.
1	37	5.63	208.31
2	40	5.62	224.80
2	40	5.64	225.60
3	40	5.78	237.20

We have now still to consider a very important question, namely, how much coke and lime are necessary to produce one pound of carbide. The formation of carbide taking place according to the following formula:

$$\underset{56}{CaO}+\underset{36}{3C}=\underset{28}{CO}+\underset{64}{CaC_2}$$

0.563 pound of carbon and 0.875 pound of calcium oxide are

[1] Of 92.17 per cent. of carbon.

theoretical necessary to yield one pound of carbide. The carbide of five cubic feet of gas per pound contains, however, free calcium oxide. We therefore might expect that more calcium oxide and less carbon are used. In practice, however, some calcium oxide and carbon are volatilized or burned. For a succession of experiments we have weighed the mixture that was put into the furnace and that which was taken out and analyzed both. We have experienced considerable trouble in weighing the red hot material accurately and in obtaining fair samples. We have therefore not been able to observe as to how far the consumption of calcium oxide and of carbon is influenced by the circumstances that alter the quantity and quality of the product. We found, however, that less mixture is used if properly stoked and if the arc is kept covered. We found also that the losses of carbon are always more considerable than those of calcium oxide.

TABLE VII.

Number of experiment.	Amount of CaO put into the furnace.	Amount of C put into the furnace.	CaO obtained from the furnace.	C obtained from the furnace.	Amount of CaO used.	Amount of C used.	Production of clean carbide.	Amount of CaO per pound of carbide.	Amount of C used per pound of carbide.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lb.
1	675	448	417	270	258	178	195	1.32	0.91
2	739	463	415	242	324	221	285	1.13	0.78
3	859	557	601	375	258	182	190	1.36	0.96
4	612	402	415	262	197	140	190	1.04	0.74
5	851	491	598	282	353	209	280	1.26	0.75
6	906	577	478	280	428	297	375	1.14	0.79
7	1067	699	420	238	647	461	555	1.17	0.83
8	552	375	253	167	299	208	223	1.34	0.95
9	374	211	207	115	167	96	132	1.27	0.73
10	675	461	244	134	431	327	345	1.25	0.95
							Average	1.228	0.837

TABLE VIII.

Number of experiment.	Mixture into the furnace. CaO.	C.	Mixture out of the furnace. CaO.	C.
	Per cent.	Per cent.	Per cent.	Per cent.
1	54.70	36.32	57.01	36.89
2	54.51	34.18	57.29	33.36
3	56.23	36.46	57.00	35.62
4	55.66	36.51	55.47	35.02
5	59.70	34.43	58.16	32.94
6	56.65	36.09	55.60	32.61
7	55.44	36.32	54.93	31.09
8	50.64	34.43	51.81	34.29
9	52.08	29.39	52.09	28.90
10	49.34	33.85	41.45	28.27

The average figures of table VII are rather high, for where much coke and lime have been used this is certainly partly due to losses of material by weighing into and out of the furnace and also by insufficient stoking. In the King furnace, the under part of which shuts hermetically tight and excludes draft, and which is stocked mechanically, the amount of coke and lime necessary for making one pound of carbide will certainly be much reduced. In the figures given in table VII we have left the outside coating out of the calculation. In a plant where the acetylene gas is generated at once from the carbide it would pay to use this coating also for making gas. From table VII we see that a very large percentage of the mixture is not acted on by the arc. We have, however, reduced this amount to one-third of the mixture and could reduce it still more without either injuring the furnace, the quantity and quality of the carbide, and without increasing the amount of carbon and lime necessary for making one pound of carbide. In the furnace used in Spray the inside is square instead of octagonal and the dimensions are rather too large. We therefore feed more material into the furnace than is necessary.

Besides coke we have used several other carbonaceous materials for making carbide. We have used soft coal, anthracite, charcoal, pitch, tar, rosin, and asphalt, and obtained in all cases carbide. Most of these materials are not of sufficient importance to be taken into consideration and we will only add some words about the first three.

Charcoal, owing to its small percentage of ash, yields a very pure carbide. The only drawback, besides its price, is that it is so light that the gases carry if off to a considerable amount. It is therefore necessary to add from five to ten per cent. more carbon to the mixture if charcoal is used than if coke is used.

We used a soft coal which contained volatile matter 19.84 per cent. and ash 1.48. The mixture with soft coal gave a terrific blaze. The carbide was covered with a large amount of very porous slag in which there was much graphite. The average of results of two runs are: 641 pounds per horse power in twenty-four hours and 4.33 cubic feet of gas per pound, which equals 27.75 cubic feet of gas per horse power in twenty-four hours.

We used anthracite coal, which contained volatile matter 7.95 per cent. and ash 4.02 per cent. We made two runs with slaked and two with unslaked lime. There was no appreciable difference in the use of slaked and unslaked lime. The average result of the four runs: 7.64 pounds per horse power in twenty-four hours and 4.03 cubic feet of gas per pound, which equals 30.79 cubic feet per horse power in twenty-four hours. These results are much lower than those obtained with coke. We can not therefore recommend the use of either anthracite or soft coal for making carbide. The superiority of coke and charcoal over anthracite is probably due to the porosity of the former materials, which must facilitate the volatilization of the carbon in the electric arc, which probably must precede the formation of carbide.

ON THE ACTION OF WAGNER'S REAGENT UPON CAFFEINE AND A NEW METHOD FOR THE ESTIMATION OF CAFFEINE.

BY M. GOMBERG.

Received February 10, 1896.

THE use of iodine in potassium iodide as a general qualitative reagent for alkaloid dates as far back as 1839.[1] It was, however, R. Wagner[2] who first employed it for the quantitative estimation of vegetable bases, and this solution has since been known as Wagner's reagent. He based his con-

[1] Bouchardat: *Compt. rend.*, 9, 475.
[2] *Ding. poly. J.*, 161, 40: *Ztschr. anal. Chem.*, 1, 102.

clusion upon trials with solution of quinine and cinchonine, showing that under approximately similar conditions they always require the same amount of iodine for complete precipitation. Hence empirical factors could be established which would enable one to use a standard solution of iodine for the titration of all such alkaloids as form insoluble superiodides. The method, however, was not frequently employed, for the reason that there was no experimental proof as to the constancy of composition of the precipitates. Moreover, it was noticed that some of the precipitates give up a portion of their iodine to water, *i. e.*, they are not completely insoluble. Hence concordant results could not be obtained. Later, Schweissinger[1] applied this method to the estimation of strychnin and brucine. His results have led him to the conclusion that while the method is very satisfactory for strychnine, it is far from being so for brucine. Recently Kippenberger,[2] in his research upon the isolation and separation of alkaloids for toxicological purposes, has reviewed the subject of the action of Wagner's reagent upon alkaloids, and gives considerable prominence to this as one of the best methods for the estimation of the vegetable bases. His method of procedure was practically the same as that first proposed by Wagner. The alkaloid is dissolved in acidulated water, and to the solution a tenth or twentieth normal solution of iodine in potassium iodide is gradually added until all the alkaloid is precipitated and the supernatant liquid shows a slight excess of iodine. Instead of filtering and washing the precipitate, as was done by Wagner and Schweissinger, Kippenberger allows the precipitate to settle, and either decants or filters off an aliquot portion of the mother liquid for the estimation of iodine not taken up by the alkaloid. The estimation of iodine is always done by means of a standard solution of sodium thiosulphate.

It has been usually assumed, for reasons not entirely clear, that the composition of the precipitates is $AlK.HI.I_2$, *i. e.*, diiodides of the hydriodides of the alkaloids are formed. Of the three atoms of iodine only two can be estimated directly by titration with sodium thiosulphate. The hydriodic acid is supposed to come from the potassium iodide, while the two "superio-

1 *Arch. d. Pharm.*, 64, 615, *1885*.
2 *Ztschr. anal. Chem.*, 34, 317; 35, 10.

dine" atoms are furnished by the free iodine dissolved in the potassium iodide. The quantity of an alkaloid precipitated by a known volume of Wagner's reagent is calculated on this assumption, 2I : molecular weight of alkaloid : : amount of iodine taken up : x = amount of alkaloid. Schweissinger found that the method of calculation agrees entirely with the theoretical figures for strychnine. Kippenberger has called into question the correctness of this mode of calculation. He, too, assumes that the composition of the precipitates is to be represented by the formula AlK.HI.I_2, but he claims that all three atoms of iodine are supplied by the free iodine, and none by the potassium iodide. Therefore the calculation of the amount of alkaloid precipitated is to be done, according to Kippenberger, by the use of the proportion, 3I : molecular weight of alkaloid : : amount of iodine taken up : x = amount of alkaloid.

The hydriodic acid, it is supposed by Kippenberger, results from the interaction of iodine and water,

$$2I + 2H_2O = 2HI + H_2O_2,$$

a reaction which is facilitated or induced by the avidity of the alkaloids to form insoluble periodides of the hydriodides. His reasons for assuming that such a peculiar reaction takes place under the simple conditions of precipitation, are too lengthy to be given here. All his arguments rest upon the assumption that all alkaloids form periodides of uniform composition, Alk.HI.I_2, and that the same alkaloid gives always the same periodide. Now, there is no reason, *a priori*, why this should be the case. Jörgenson's[1] extended researches show that different alkaloids, when treated under apparently the same conditions, give periodides of entirely different compositions. Thus, morphine gives with Wagner's reagent Alk.HI.I_2;[2] codeine furnishes with excess of Wagner's reagent Alk.HI.I_4; and caffeine, as will be shown, gives Alk.HI.I_4, etc. It is safe to say that not until we ascertain exactly the composition of the different periodides as produced under the conditions of titrations, will the use of Wagner's reagent for quantitative purposes be placed upon a sound basis.

[1] *J. prakt. Chem.*, *1870-78*, [2], 2, 433, etc.
[2] Jörgenson, 1870 : *J. prakt. Chem.*, [2], 2, 438.

I have dwelt at such length upon this subject, because the method for the estimation of caffeine presently to be described, is based upon experimental evidence which is entirely contradictory to Kippenberger's conclusions. Whatever the cause may be with other alkaloids, his theory as to the production of hydriodic acid from iodine and water, does not hold good in the case of caffeine.

Wagner, in describing his method, gives a list of alkaloids which are completely precipitated by iodine solution, and also mentions that "caffeine, theobromine, piperine and urea are not precipitated at all."[1] His statement, so far at least as caffeine is concerned, has stood since then uncontradicted. It has found its way not only into standard treatises and text-books,[2] but even into periodical literature of recent date. As late as 1894, Kunze,[3] in reviewing the chemistry of caffeine and theobromine, calls attention to this peculiarity of the two alkaloids. The non-precipitation of caffeine by Wagner's reagent has come to be recognized as a distinguishing feature of this alkaloid from almost all other vegetable bases.

And yet this is entirely contrary to actual facts. Instead of forming an exception, caffeine conforms to all the requirements[4] necessary in the application of this test. It is well known that most of the alkaloids as such are insoluble, or only very slightly soluble in water; they require the presence of some acid for their complete solution. In other words, alkaloids in the form of their salts, are soluble in water. Whenever Wagner's reagent is applied for the precipitation of an alkaloid, it is always applied to a solution of some salt of it, preferably acidulated with sulphuric or hydrochloric acid. Therefore, even when strictly neutral salts of alkaloids are employed, there is still the possibility of the formation of hydriodic acid, or rather of the hydriodides of the alkaloid, as for instance, $Alk.HCl + KI = Alk.HI + KCl$.

1 *Loc. cit.*, 41.

2 Prescott, Organic Analysis, p. 80; Allen, Comm. Organic Analysis, Vol. 3, (2). 481: Fluckiger, Reactions, (Nagelvoort's Translation), p. 26; not affected by Wagner's reagent in either neutral or acid solutions. Dragendorff, 1888. Ermittelung von Giften. says that caffein gives a dirty brown precipitate. From the text it is not improbable he used iodine in hydriodic acid.

3 *Ztschr. anal. Chem.*, 33, 23.

4 This test is perhaps most frequently made in a neutral solution, representing, as customary state, free caffeine and *normal salts* of other alkaloids.

'he hydriodide thus produced is at once precipitated as a peridide. Now, it so happens that caffeine is tolerably soluble in rater, and it has become customary to work with solutions of affeine as a free alkaloid, and not in the form of its salts. The uestion as to whether solutions of free alkaloids are precipitated rith Wagner's reagent has not, to my knowledge, been studied. [y preliminary experiments in that direction show that at least ome alkaloids (morphine, atropine, strychnine, etc.), are preipitated. I have not examined yet whether these periodides re identical in composition with those produced from the salts f the alkaloids. But so far as caffeine is concerned, it is true hat a neutral solution of it gives no precipitate when treated with a olution of iodine in potassium iodide. When however the addiion of Wagner's reagent is either followed or proceeded by the ddition of some dilute acid, there is at once thrown down a ark-reddish precipitate, remaining amorphous even on long tanding.[1] The composition of this periodide is, as will be shown, $C_8H_{10}N_4O_2.HI.I_4$. It was obtained for analysis in many different rays—by using either caffeine or iodine in excess, and by mploying different acids. The periodide produced is, however, lways of the same composition. The precipitates were allowed o settle, filtered by means of a pump, washed with water to emove the excess of potassium iodide, dried on porous plates, nd finally in a *vacuum* over sulphuric acid.

I. This sample was obtained by slowly adding a solution of odine in potassium iodide to a solution of caffeine acidulated rith sulphuric acid. The iodine was added until the supernaant liquid was decidedly red. The whole was allowed to stand hree hours, filtered, washed and dried as described above. The otal iodine was estimated in the usual way, *i. e.*, by suspending weighed sample in water, adding sulphurous acid solution, hen silver nitrate and nitric acid; filtered, washed and dried. The "exterior" iodine, *i. e.*, the iodine not as hydriodic acid,

[1] Almost the same can be said of theobromine, making allowance for the difference of solubility of the alkaloid in water. A saturated solution of it (containing one part of theobromine to 1600 of water) gives no precipitate with Wagner's reagent, but on the addition of a drop of acid there separates in a short time a crystalline periodide. Contrary to usual statements, I find that theobromine in acid solutions gives a heavy precipitate with Wagner's reagent, of a peculiar dirty-blue color.

was estimated by direct titration with standard sodium thiosulphate.

0.2002 gram gave for total iodine 0.2785 gram AgI.
0.2358 " " " exterior " 0.1433 gram I.

......

II. This sample was obtained by adding to an acidulated solution of caffeine enough iodine to precipitate about one-half of the caffeine present.

0.2563 gram gave for total iodine 0.3591 gram AgI.
0.1659 " " " exterior " 0.0997 gram I.

III. A neutral solution of caffeine was mixed with an excess of Wagner's reagent, and to the mixture dilute sulphuric acid was gradually added so long as a precipitate was produced.

0.4039 gram gave for total iodine 0.5668 grams AgI.
0.1424 " " " exterior " 0.0866 gram I.

IV. Filtrates from I and III, on long standing, gave a deposit of dark-blue needle-like crystals, which were collected, washed and dried as before.

0.7884 gram gave for total iodine 1.1064 gram AgI.
0.4450 " " " exterior " 0.2685 gram I.

V. This was obtained by recrystallizing the amorphous precipitate from methyl alcohol.

0.2890 gram gave for exterior iodine 0.1756 gram I.

VI. Obtained by recrystallizing the amorphous periodide from hot ethyl acetate.

0.4807 gram gave for total iodine 0.6709 gram AgI.
0.2777 " " " exterior " 0.1622 gram I.

Calculated for [illegible]	Per cent.	Found. I.	II.	III.	IV.	V.	VI.
[illegible]	[illegible]	75.12	75.66	75.84	75.83	....	75.40
[illegible]	[illegible]	[illegible]	[illegible]	60.81	60.34	60.76	60.22

[illegible] lution of sul-

furnished the iodine, and the compound thus obtained has the composition, according to Tilden, $2(C_8H_{10}N_4O_2HI.I_2).3H_2O$. It is a lower periodide than the one which is obtained when iodine dissolved in potassium iodide is directly added to caffeine, as the latter has the composition $C_8H_{10}N_4O_2.HI.I_4$. Tilden also mentions that by the addition of alcoholic iodine to a solution of caffeine in weak sulphuric or hydriodic acid, he obtained a deposition of black granules, which upon analysis furnished about seventy-five per cent. of total iodine. He says that it probably consists of a compound containing nine atoms of iodine. But there is hardly any doubt that he had the tetra-iodide of caffeine hydriodide.

Properties. When dry the periodide is a violet-blue amorphous powder melting at 213° C. When moist it rapidly losses iodine on exposure to air. It is permanent when dry and suffers but slight loss when heated to 100° C. Two grams heated for four hours at that temperature lost only 0.027 gram = 1.33 per cent. It losses but very little of its iodine when suspended in water, giving up enough iodine to saturate the liquid. The presence of potassium iodide in the water favors the liberation of iodine, but even then it is but slight. The periodide dissolves readily in alcohol, especially when heated, with considerable decomposition into the free base and iodine. It is more soluble in methyl alcohol and suffers less decomposition in that solvent. It can be obtained from methyl alcohol, on spontaneous evaporation of the solvent, in the form of beautiful crystals, with a metallic dark-bluish luster. When examined under the microscope the crystals appear to consist of six-sided prisms. Ether, whether cold or warm, decomposes it but slightly. The periodide is insoluble in chloroform, carbon disulphide and benzene. It is soluble without decomposition in hot ethyl acetate from which it separates on cooling as a dark granular crystalline deposit, which melts at 215° C.

Limits of Precipitation. Like most alkaloids, caffeine is precipitated by Wagner's reagent even from very dilute solutions of the base. Although not characteristic, it is yet as delicate a test for caffeine as we have. The limits of precipitation, under the influence of different acids, will appear from the following

means of Wagner's reagent. This method gives very satisfactory results, as nearly theoretical as could be expected. I am indepted for the analytical data of the subjoined table to Mr. James W. Knox, holder of the Stearns' Fellowship in the School of Pharmacy. The method of procedure employed by us was practically the same as that used by Kippenberger. Definite volumes of acidulated solutions of caffeine were precipitated with a known volume of iodine in potassium iodide. After complete precipitation an aliquot portion of the supernatant liquid was obtained, either by decantation or filtration, and the excess of iodine was estimated by titrating against a tenth normal solution of sodium thiosulphate. The precipitation is best performed in a tall test-tube on foot, and the solution for titration is removed directly by immersing the end of the burette into the liquid and applying suction at the upper end. When it is desirable to filter off an aliquot portion, a filter of glass-wool and asbestos gives very satisfactory results.

We have tested the method on solutions of caffeine acidulated with sulphuric acid, the solutions being of different strengths, namely: containing 0.25 per cent. of caffeine, 0.50 per cent., 0.75 per cent., and 1.00 per cent., respectively. We have varied in different series of experiments the amounts of Wagner's reagent, employing just the theoretical quantities, a small and large excess above that, as well as the quantities below those required by the theory. Columns I, II, III, and IV give the results obtained by allowing the solutions to stand for an hour before decanting an aliquot portion for titration; column V shows the results obtained when the liquid for titration was filtered off within five minutes after the addition of Wagner's reagent. The results are calculated on the basis that the periodide has the composition $C_8H_{10}N_4O_2.HI.I_4$. The amount of alkaloid is calculated from the amount of iodine used up, by the formula,

$$4I : C_8H_{10}N_4O_2 : : 506 : 194 ;$$

i. e., one part of iodine represents 0.3834 parts of caffeine. Or, one cc. tenth normal iodine = 0.00485 grams caffeine.

The results presented below show that the estimation of caffeine by this method is very exact. The best results are obtained

Wagner's reagent employed.	I. Solution containing 0.25 per cent. of caffeine.			II. Solution containing 0.50 per cent. of caffeine.			III. Solution containing 0.75 per cent. of caffeine.			IV. Solution containing 1.00 per cent. of caffeine.			V. Solution containing 0.50 per cent. of caffeine.		
	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.
Theoretical quantity + 2 cc.	0.0600	0.0591 0.0589	98.33	0.1200	0.1175 0.1175	97.82	0.1500	0.1481 0.1471	98.40	0.1200	0.1182 0.1179	98.38	0.1200	0.1154 0.1165	96.78
1⅓ theoretical quantity.	0.0750	0.0749 0.0749	99.88	0.1200	0.1191 0.1189	99.17	0.1500	0.1489 0.1485	99.13	0.1200	0.1191 0.1187	99.12	0.1200	0.1196 0.1197	99.75
Twice the theoretical quantity.	0.0500	0.0502 0.0506	100.80	0.0800	0.0805 0.0789	99.63	0.1200	0.1184	98.67	0.1100	0.1091 0.1091	99.18	0.0800	0.0802 0.0791	99.63
One-half of the theoretical quantity.	0.0750	0.0363 0.0363	48.40	0.1600	0.0794 0.0794	49.62	0.2250	0.1107	49.20	0.2000	0.1067 0.1067	53.35	0.1600	0.0791 0.0791	49.44

when iodine is in considerable excess, as is evident from the figures obtained where one and one-third and twice the theoretical quantities of Wagner's reagent were used. All the results in the table were obtained on solutions of caffeine acidulated with sulphuric acid, the acidulation being tolerably strong, about one cc. of the concentrated acid to fifty cc. of the liquid. Experiments upon the influence of the acid indicate that a large excess of sulphuric acid interferes to some extent with the reaction. The amount of recovered caffeine falls as low as ninety-five per cent. of the quantity taken, when four cc. of the concentrated acid to fifty cc. of the liquid are used. The results are also not very uniform and concordant. The fact that the precipitation of caffeine by Wagner's reagent is more delicate in presence of hydrochloric acid than any other acid would make it advisable to employ that acid in quantitative estimation of the base by iodine.

This method could easily be employed for the estimation of the alkaloid in caffeine-bearing drugs. Of course, it is necessary to have the final solution of the alkaloid in water as free as possible from other substances that may be precipitated by Wagner's reagent. The estimation of caffeine by this method is likely to give higher results than have hitherto been obtained. The following procedure is recommended:[1] The drug is thoroughly digested with water for some time, by the aid of heat, cooled, and made up to a definite volume, and filtered. An aliquot portion of the filtrate is treated with lead acetate, the precipitate allowed to settle, and filtered. The whole of the filtrate, or a given portion of it, is treated with hydrogen sulphide to remove the lead, and filtered. This filtrate, after boiling off the hydrogen sulphide, is divided into two equal portions, and each treated with a definite volume of the standard iodine solution,—the first portion without the addition of any mineral acid, the second with the addition of hydrochloric or sulphuric acid. After five to ten minutes' standing the excess of iodine is estimated in each of the two solutions, as described above. The first portion, containing no other but some acetic acid, serves to indicate whether the filtrate from the lead sulphide contains any other materials besides caffeine that are likely to be

[1] These directions are in part those given by Spencer, *1890 : J. anal. Chem.*, 4, 390.

precipitated by Wagner's reagent,— for caffeine itself is not precipitated by it even in presence of tolerably strong acetic acid. If any absorption of iodine be found in the first portion, then that quantity is to be subtracted from the amount of iodine taken up by the second portion ; the difference represents the iodine used up in the formation of the periodide of caffeine. The amount thus used up, multiplied by 0.3834, gives the amount of caffeine in that particular portion of the liquid.

ANN ARBOR, MICHIGAN.

ON THE FORMATION OF ANTIMONY CINNABAR.

BY J. H. LONG.

Received February 15, 1896.

THE composition of the pigment known as antimony cinnabar has been stated by several different formulas, as may be seen by consulting the leading hand-books of chemistry. The substance was usually considered as a mixture of sulphide and oxide or as an oxysulphide with the formula Sb_2S_2O. The formula, Sb_2S_3, is found also in some of the older works, and Baubigny[1] has shown that this is undoubtedly the correct one. Experiments made by myself and described in this Journal, in February, 1895, led me to adopt the same formula.

The compound is usually prepared by boiling a solution of antimony chloride or tartrate with sodium thiosulphate or crude calcium thiosulphate. As obtained from the acid solution of the chloride, the product is not pure and not of constant composition, being frequently mixed with oxychloride. This mixture is a mechanical one and analysis made from it has no value in establishing a formula. The precipitate obtained by boiling a mixture of pure solutions of tartar emetic and sodium thiosulphate, on the other hand as a constant composition, and numerous analyses I have made of it in the past year lead to the formula already given.[2]

By analogy with other formulas established in the paper referred to I suggested there that the reaction between the tartrate and thiosulphate may be represented by this equation :

[1] *Compt. rend.*, October 22nd, 1894.

[2] *Loc. cit.*

$$2KSbOC_4H_4O_6 + Na_2S_2O_3 + H_2O = 2KNaC_4H_4O_6 + Sb_2O_3 + H_2S_2O_3,$$

the oxide and thiosulphate then acting on each other to form sulphide:

$$Sb_2O_3 + 2H_2S_2O_3 = Sb_2S_3 + 2H_2O + SO_2 + 5O.$$

The oxygen and sulphur dioxide are not liberated as such but held as polythionates with the excess of thiosulphate used.

To throw further light on the reaction I have attempted the formation of the cinnabar by other methods. While the product is sulphide of antimony, it appears that it can be made with its characteristic color only by the decomposition of a thiosulphate. All attempts to obtain the true precipitate by action of hydrogen sulphide or alkali sulphides and sulphur dioxide on antimony solutions failed. The only body formed was the amorphous sulphide, often mixed with sulphur. On the other hand, by the action of a neutral or acid mixture of an antimony compound and a thiosulphate on each other, the cinnabar red product is the only one formed. If the mixture is made alkaline by the addition of a drop or two of ammonia water, no sulphide whatever precipitates. A small amount of hydrated oxide of antimony separates, but the decomposition of the thiosulphate is prevented. On the addition, now, of enough weak acid to neutralize the ammonia a yellow precipitates soon appears, but this speedily changes to deep bright red. The formation of the true cinnabar seems to begin by the appearance of a yellowish intermediate product, which is compatible with the above equations.

In this connection it is interesting to note the behavior of pure antimony trioxide with solutions of thiosulphate. The reaction of the latter with a soluble antimony compound is comparatively rapid, and the experiments were made to show the action of the oxide under the same conditions. It was found that the latter, when added to a strong or weak neutral thiosulphate solution is unable to effect a decomposition, in the cold or by application of heat. When the mixture is boiled the oxide remains perfectly white. This is true even after heating in an autoclave under a pressure of eighteen atmospheres.

It was found, however, that with the addition of a little acid to the mixture of oxide and thiosulphate, a reaction followed after a time, although it never became complete. In a series of experiments a constant weight, 0.576 gram, of the pure precipitated, washed, and dried oxide was taken and mixed with water and a constant weight of sodium thiosulphate in solution, in each case 0.992 gram of the salt. Definite volumes of half normal hydrochloric acid were then added and water enough to make the total volume fifty cc. in each case. The mixtures were made in small Erlenmeyer flasks, loosely stoppered, and were very frequently shaken. The amounts of hydrochloric acid taken are given in the table below. The reactions became apparent only after several minutes, and after five hours, had advanced so far in the mixtures numbered one and two, that the products had become orange. The reactions in the other flasks were less marked, but later became strong. The mixtures were made on October 7th and were shaken many times daily through two months, in fact, as long as any change of color in them was noticed. On December third the amount of sulphide of antimony present was found by the method of Rivot, oxidation by chlorine after preliminary treatment with strong potassium hydroxide solution. The sulphur is found as sulphate and the amount of sulphide formed in each case is shown by the table.

No.	Amount of Sb_2O_3.	$Na_2S_2O_3$.	$\frac{N}{2}$ HCl.	H_2O.	$BaSO_4$ found.	Sb_2O_3 converted.
1	0.576 gram.	0.992 gram.	2 cc.	48 cc.	0.155 gram.	0.064 gram.
2	0.576 "	0.992 "	4 "	46 "	0.293 "	0.121 "
3	0.576 "	0.992 "	8 "	42 "	0.384 "	0.158 "
4	0.586 "	0.992 "	12 "	38 "	0.427 "	0.176 "
5	0.576 "	0.992 "	16 "	34 "	0.454 "	0.187 "

In mixtures one and two no evolution of sulphur dioxide could be detected by the odor or by tests, but in the others it was apparent, weak in 3 and strong in 4 and 5. No free sulphur was precipitated in any case, or at any rate could not be found in the final product. Although but a small part of the oxide was actually converted the color of the products in mixtures 1 and 2, was a deep cinnabar, and perfectly characteristic. The amounts of sulphide formed or of oxide converted are not

proportional to the volumes of acid used, and are much less than should be found on the assumption that the reaction begins by the production of antimony chloride from the oxide. If this were true, the sulphide formed by means of the soluble thiosulphate should increase with the acid taken. The reaction appears to take place between the oxide and thiosulphuric acid liberated by the hydrochloric acid, as was suggested by several experiments. In one case 0.500 gram of antimony oxide was treated with ten cc. of half normal hydrochloric acid and thirty cc. of water, as before, and allowed to stand twenty minutes, with frequent shaking. The mixture was then filtered and to the filtrate one gram of sodium thiosulphate in ten cc. of water was added. In a short time a precipitate of sulphur formed, perfectly light colored, showing the absence of even a trace of the antimony. The rapidity with which the thiosulphate was decomposed showed that the hydrochloric acid taken must be in the filtrate and not in the residue, as oxychloride for instance. Titration of the filtrate showed this in a similar case. In a second experiment the acid and thiosulphate, in amounts equal to those of the last experiment, were mixed, and after the lapse of one minute the now opalescent mixture was added to some antimony oxide. Although the reaction between the first substances had gone into its second stage, showing that the hydrochloric acid was now certainly in combination, a precipitation of antimony sulphide began almost immediately and in a short time the cinnabar color was distinct.

Thiosulphuric acid is usually spoken of as quite unstable, but Landolt has shown[1] that in dilute solutions it may exist many seconds, even minutes. The interval before precipitation is lengthened by dilution. If decomposition begins in presence of compounds of the heavy metals, a sulphide, sulphur dioxide, and polythionates may form. A large excess of thiosulphuric acid is necessary to complete the reaction in this manner, as suggested by the experiments of Vortmann.[2]

In experiment No. 1 of the table above the amount of hydrochloric acid taken is just one-eighth of that necessary to complete this reaction with the thiosulphate :

[1] *Ber. d. chem. Ges.*, 16, 2958.
[2] *Ber. d. chem. Ges.*, 22, 2309.

$$2HCl + Na_2S_2O_3 = 2NaCl + H_2S_2O_3.$$

By full conversion enough acid would be liberated to complete the equation assumed at the beginning,

$$Sb_2O_3 + 2H_2S_2O_3 = Sb_2S_3 + 2H_2O + SO_2 + 5O,$$

with the amounts of oxide and thiosulphate taken. It follows, therefore, that not over one-eights of the antimony oxfde taken should be found converted into sulphide, and the result of the experiment shows slightly less than this. According to this theory we should have 0.072 gram of oxide changed. The test shows 0.064 gram. In the second and following experiments the amount of oxide converted is relatively still less. The acid taken in the last experiment is sufficient to decompose all of the thiosulphate and thus permit the conversion of all of the oxide. But the result shows that slightly less than one-third the oxide has been changed. In the first experiments no escape of sulphur dioxide was noticed, while in the last it was quite marked and this fact has doubtless some connection with the low amount of sulphide formed. The reaction which takes place in a weak solution of thiosulphuric acid is evidently different from that in the strong solution, inasmuch as the greater portion of the sulphur seems to be given off as sulphide in the one case and as sulphur dioxide in the other.

In the somewhat similar reaction with arsenious oxide Vortmann[1] suggests this equation,

$$As_2O_3 + 9H_2S_2O_3 = As_2S_3 + 3H_2S_4O_6 + 3SO_2 + 6H_2O,$$

in which but one-sixth of the sulphur present is used to form sulphide. By increasing the amount of hydrochloric acid added to the thiosulphate the decomposition of the latter is hastened.

It is possible that after a time, with increased liberation of sulphur dioxide the formation of sulphide may be retarded, as was suggested by this experiment. I mixed half a gram of the antimony oxide with one gram of sodium thiosulphate in ten cc. of water, and added ten cc. of half-normal hydrochloric acid and thirty cc. of moderately strong solution of sulphur dioxide, free from air. By using water instead of the last solution, precipitation would appear in a few minutes, but in this case it was

[1] *Loc. cit.*

oon appeared and in a short time the whole product
to be cinnabar. The reaction is doubtless aided by the
loric acid liberated by the decomposition of the oxychlo-
presence of water. The acid in turn attacks the thiosul-
and so the process becomes continuous and rapid. These
as are all much hastened by application of heat and the
ative relations are also altered, but at a temperature of
thiosulphuric acid seems to be the active precipitating
n the cases investigated.

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PERHALIDIES OF CAFFEINE.

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Received February 23, 1896.

I. INTRODUCTION.

formation of periodides by organic bases has been known as far back as 1839.[1] Their methods of prepara- ieir composition and properties have been subjects of gation at different periods since then. Jörgensen,[2] in made a complete review of the subject, and has contributed list of new periodides. In 1887, Gunther[3] made a com- of all the periodides known up to that time, and reported new ones. More recently Prescott[4] offered a classification now periodides of both organic and inorganic bases, pre- at the same time a history of the principal advances in dy of the subject.

hardly necessary. We know of no property, as to composition or stability, which is characteristic of one class of the periodides, and is not shared equally well by the other. At one time, Dittmar[1] thought to have found such a distinguishing reaction in the formation of chloriodides of the bases. According to him, it is only the bases of pyridine structure that are attacked by chloride of iodine, with the formation of chloriodides, RNCl.I. Yet it has been shown[2] previously to his report that this is not the case. Later, Ostermayer[3] reported the formation of such a chloriodide of caffeine, and recently Pictel and Krafft[4] obtained by the action of trichloride of iodine a similar chloriodide of trimethylamine.

All the periodides of primary, secondary, and tertiary ammonium salts, including those of pyridine and its derivatives, contain hydriodic as the salt-forming acid, and the "periodine" is supposed to be linked to the iodine of this acid. The iodine of the acid, being linked directly to the nitrogen of the base, is not affected by reducing agents, such as sulphurous acid, sodium thiosulphate, nascent hydrogen, etc., while the "periodine" is readily attacked under such treatment, and yields hydriodic acid. The constitution of quaternary ammonium periodides, including those of the quaternary pyridine salts, is entirely similar to that of the tertiary class, the hydrogen of the acid being replaced by an alkyl. The following formulas will make this clear:

$$R'''N\lt_{I.I_n}^{H}, \quad \text{periodides of tertiary ammonium salts.}$$

$$R'''N\lt_{I.I_n}^{R}, \quad \text{periodides of quaternary ammonium salts.}$$

The organic bases are also capable of forming other halogen additive compounds, besides the simple periodides. These can be classified as follows:

1. Compounds wherein iodine or bromine is linked directly to the nitrogen without the intervention of a halogen acid, such as

[1] *Ber. d. chem. Ges.*, **18**, 162, *1885*.
[2] *J. Chem. Soc.*, **19**, 145, *1866*.
[3] *Ber. d. chem. Ges.*, **18**, 2298, *1885*.
[4] *Bull. Soc. Chim.* [3], **7**, 72, *1892*.

pyridine tetraiodide, $C_5H_5N.I_4$,[1] quinoline tetrabromide, $C_9H_7N.Br_4$.[2]

2. Those obtained by the action of monochloride[3] and trichloride[4] of iodine upon bases. They contain both chlorine and iodine linked directly to the nitrogen. Their structure can be represented by the general formula $R'''N<^{Cl}_{I}$. These compounds still retain the power of forming salts by union with acids, as $(R'''NClI).HCl$.

3. Periodides wherein the "periodine" is linked to another halogen not iodine. These are few in number, and are all on the quarternary ammonium type, $R'''N<^{R}_{Br.I_n}$.

4. Periodides containing another acid[5] in addition to hydriodic acid, such as in herapathites, periodo selenites, phosphates, chlorides, etc. But as each contains hydriodic acid, Jörgensen legitimately infers that the "periodine" is, in all probability, linked to this acid and not to the other.

5. Perbromides of the hydrobromide of bases. Only very few of these have been reported, although it is well known that a great number of alkaloids are precipitated by bromine dissolved in hydrobromic acid. Pyridine,[6] quinoline,[7] and nicotine[8] form such perbromides.

All the perhalides of organic bases, so far reported, (except the simple periodides) can be referred to one of these five classes. And yet it can hardly be doubted that periodides and perbromides of other salts than hydriodides and hydrobromides respectively, are capable of existence. I have not been able to find any reports upon periodides in which either hydrochloric or hydrobromic acid has exactly the same function as hydriodic acid has in the simple periodides. Such derivatives can only be prepared when precautions are taken to strictly insure the absence of hydriodic acid during the preparation of the periodide,

1 Dafert, *Monatsh. Chem.*, 4, 509, *1883*; Prescott and Trowbridge: This Journal, 17, 865.
2 Grimaux, *1882*: *Bull. Soc. Chim.*, 38, 124.
3 Dittmar, *1885*: *Ber. d. chem. Ges.*, 18, 162.
4 Pictel and Krafft: *loc. cit.*, 72.
5 Jörgensen, *1876*: *J. prakt. Chem.* [2], 14, 213, 356; 15, 65.
6 Grimaux: *Bull. Soc. Chim.*, 38, 127, *1882*.
7 *Ber. d. chem. Ges.*, 19, 2766, *1886*.
8 *Ann. Chem.* (Liebig), 131, 260.

and this has never been the case in the methods that have hitherto been employed for that purpose. In the following pages will be found a description of such periodides of caffeine, which have been obtained by a method different from those that have been described. The compounds have all been prepared by substituting chloroform for alcohol as the medium of reaction, thus eliminating the action of iodine upon alcohol at higher temperatures, and the subsequent formation of hydriodic acid. Not only periodides, but perbromides of similar composition and constitution have been prepared by this method. The method is, indeed, of very general application for such purposes. Periodides of hydrobromides and hydrochlorides of the following bases have thus been obtained: Quinine, quinidine, cinchonine, cinchonidine, strychnine, brucine, atropine and quinoline (of the hydrobromide only).

It has been said of the periodides that "if they contain, as their behavior has been interpreted to imply, for every atom of iodine that is linked to the base, a number of atoms of iodine linked only to iodine, they offer a striking example of the influence of a basal group upon iodine atoms to which it is not linked." This naturally suggested the question, whether this influence is or is not proportional to the basal power of the group; in other words, is the number of iodine atoms thus attached under given conditions, as index of the basic power of the different bases? Again, we might ask whether the same influence is exerted in the same degree upon bromine. And furthermore, we might inquire, in how far does the nature of the halogen acid modify the influence of the base upon the "periodine," or "perbromine?" The following pages give an account of such a comparative study of perhalides of one base, caffeine.

II. PERIODIDES OF CAFFEINE.

Caffeine Hydriodide Diiodide, $C_8H_{10}N_4O_2.HI.I_2$.—Tilden reported in 1865,[2] that when a solution of caffeine in dilute alcohol, containing some hydriodic acid, is exposed to sunlight, there appears in a few days a deposit of beautiful crystals, with a metallic greenish appearance, unstable, readily decomposing

1 Prescott, 1885: This Journal, 17, 775.

2 *J. Chem. Soc.*, 18, 99.

even at the water-bath heat. He assigned to the compound the formula $(C_8H_{10}N_4O_2.HI.I_2)_2.3H_2O$, and this agress closely with the results of his analysis. In repeating the experiment, I find that under certain conditions a diiodide is formed, but the results of my analysis show no water of crystallization. Again, the diiodide is formed only when the formation of the crystals is tolerably rapid, as when the solution is kept in a warm place and exposed to direct light, conditions favoring oxidation of hydriodic acid. If, however, the liberation of iodine be very slow, yielding about a half gram of periodide in six or seven weeks, a tetraiodide is produced. The diodide, obtained as above described, was filtered on a pump, washed with water containing some hydriodic acid, dried on porous plates and finally over sulphuric acid *in vacuo*. The samples were analyzed for total iodine and for the "periodine," or, as Tilden calls it, the "exterior" iodine. The first is estimated by suspending a weighed sample in water, treating with a solution of sulphur dioxide, then precipitating with silver nitrate and nitric acid. The "periodine" is estimated by titrating with a standard solution of sodium thiosulphate. The difference between the total and "exterior" iodine is that which corresponds to the hydriodic acid. Two independent samples thus prepared gave the following results:

	Calculated for $C_8H_{10}N_4O_2.HI.I_2$.	Found. I.	II.
Total iodine	66.06	65.12	64.29
Periodine	44.04	44.04	44.18

The diiodide consists of long hexagonal prisms, with a metallic greenish luster. It decomposes readily when moist, but is quite stable when dry. When suspended in water the crystals lose their luster and become coated with a brown-red layer of the tetraiodide. It is soluble in warm alcohol with decomposition, insoluble in ether and chloroform. It melts at 171° C.

Caffeine Hydriodide Tetraiodide, $C_8H_{10}N_4O_2.HI.I_4$.—This is the periodide which caffeine usually forms when it forms any at all, except as above described. It is the most stable periodide of caffeine, and is formed under many different conditions, in both the amorphous and crystalline state. It has been obtained by the following methods:

1. When a solution of caffeine is treated with a solution of iodine in potassium iodide (Wagner's reagent), there is no visible reaction. On the addition of some mineral acid, a heavy amorphous dark-red precipitate is at once thrown down. The precipitation of caffeine in this way is quantitative, and forms the basis of a method for the estimation of caffeine.[1] The composition of this precipitate is, as I have fully described,[2] $C_8H_{10}N_4O_2.HI.I_4$. It was obtained for analysis in many different ways by varying the relative quantities of the reagents employed, but it has always proven to be of the same composition. The samples for analysis were obtained by filtering the amorphous precipitate on a pump, washing with water to remove the potassium salts, drying rapidly on porous plates, and finally *in vacuo* over sulphuric acid. The following are the results of analysis:

	Calculated for $C_8H_{10}N_4O_2.HI.I_4$.	Found. I.	II.	III.	IV.
Total iodine	76.43	75.12	75.66	75.84	....
Periodine	61.15	60.79	60.11	60.81	60.76

2. When caffeine is dissolved in chloroform and is treated with a solution of iodine also in chloroform, no formation of any periodide could be noticed, even when the mixture is allowed to stand for weeks. If into this solution dry hydriodic acid gas be now passed, there is at once precipitated an amorphous dark-red periodide, identical in composition with that described under 1. Upon analysis it gave the following figures:

	Per cent.
Total iodine	75.14
Periodine	60.23

3. When a solution of caffeine in hydriodic acid is exposed to sunlight, but the liberation of iodine is hindered either by low temperature, or the presence of some reducing agents in the solution, then the crystals that are formed have the composition of the tetraiodide, and not that of diiodide. They also have a different appearance, being short prisms of a deep blue color. Several samples obtained in this way furnished the following figures:

[1] This Journal, 18, 331.
[2] *Loc. cit.*

	I.	II.	III.	IV.
Total iodine	....	....	....	75.11
Periodine.............	60.26	59.86	59.75	60.60

4. When either caffeine hydrobromide dibromide or tetrabromide is triturated with a solution of potassium iodide in water, there is again produced the same amorphous periodide. It gives upon analyses 59.90 per cent. "of exterior" iodine.

These four different methods show the great tendency of caffeine to form the higher periodide, which is apparently more stable than the diiodide. Weak base as it is, caffeine readily forms a higher periodide than is produced under similar conditions by many other organic bases.

Properties.—The periodide in the amorphous state and when dry, is of a dark blue-red color. It is quite stable when dry, and can be heated at 100° C. for many days without any appreciable loss of iodine. When moist it readily gives off iodine. Suspended in water, it gives up sufficient iodine to saturate the liquid, and after that remains unchanged. A solution of potassium iodide removes only a little more iodine than pure water alone. The periodide cannot be recrystallized from alcohol without considerable decomposition into caffeine and iodine. It is more soluble in methyl alcohol, and if not too much heat be used in dissolving it, the periodide can be obtained unchanged on spontaneous evaporation of the alcohol in the form of dark-blue needles. Ethyl acetate is, however, the best solvent for this periodide, as the latter dissolves in acetic ether without decomposition, even when heated. On cooling, the periodide separates in fine compact crystals. It is insoluble in chloroform, ether, benzene and carbon disulphide. It melts at 215° C.

Caffeine Hydrobromide Tetraiodide, $C_6H_{10}N_4O_2.HBr.I_4$.—Caffeine forms with hydrobromic acid a salt of the following composition, $C_8H_{10}N_4O_2.HBr + 2H_2O$.[1] The salt can best be obtained in a pure state by passing dry hydrobromic acid gas into a solution of caffeine in chloroform. The white crystalline precipitate is filtered, washed with chloroform, and dried in an atmosphere free from moisture. Thus prepared it has the composition $C_8H_{10}N_4O_2.HBr$. The periodide of this hydrobromide

[1] E. Schmidt, *1881: Ber. d. chem. Ges.*, 14, 815.

can only be prepared in the absence of other halogen acids, especially of hydriodic acid. Therefore the addition of iodine as a solution in potassium iodide, to a solution of caffeine hydrobromide, is out of the question, as in such a case the periodide of the hydriodide will be formed. Nor can alcohol be successfully employed as a solvent for iodine, because this will furnish hydriodic acid, and also because the periodide of the hydrobromide itself is more or less dissociated by alcohol. This periodide is, however, readily obtained when a slow stream of dry hydrobromic acid gas is led into a solution of caffeine and iodine in chloroform. The addition of the acid must be very slow, and care must be taken to have the iodine in excess, otherwise the pure hydrobromide, or lower periodides of it will be thrown down together with the tetraiodide. In such cases redigesting the mixed periodides in a fresh solution of iodine in chloroform converts them into the tetraiodide. Further digestion shows no absorption of iodine. The periodide is filtered, washed with chloroform to remove the excess of caffeine or iodine, as the case may be, dried on porous plates, and finally in a desiccator. The "exterior" iodine is estimated by titration with sodium thiosulphate. The bromine is found by subtracting from the total mixture of silver halides, as obtained by precipitation with silver nitrate, the quantity of silver iodide corresponding to the "periodine" as found by titration. This difference represents the amount of silver bromide. The accuracy of this method was tested in several instances by actually estimating the amount of silver as such in the precipitate of the mixed halides, and from this the relative proportions of the two halogens were calculated.

The analysis of several samples furnished the following figures:

	Calculated for $C_8H_{10}N_4O_2.HBr.I_4$.	Found. I.	II.	III.
Iodine	64.79	63.56	63.91	62.28
Hydrobromine	10.37	9.63	....	....

This periodide is usually obtained as an amorphous powder. But when the addition of hydrobromic acid is very slow, it can be obtained in microscopic crystals. It is of a dark-brown chocolate color, and melts at 183° C. It is decomposed by water

but slowly, more readily, however, than the corresponding hydriodide. It dissolves readily in alcohol, with considerable decomposition. It is more soluble in methyl than in ethyl alcohol, and also with less decomposition. On evaporating the methyl alcohol the tetraiodide can be obtained in brown crystals. It can also be recrystallized from ethyl acetate. Ether removes considerable iodine, and chloroform, hot or cold, does not affect it. On exposure to air the periodide gradually, but slowly, loses iodine, and hardly any if protected from moisture. By heating to 100° C. the iodine can be driven off completely. Thus this periodide is in all respects a less stable compound than the corresponding tetraiodide of caffeine hydriodide.

Caffeine Hydrochloride Diiodide, $C_8H_{10}N_4O_2.HCl.I_2$.—Caffeine is capable of uniting with hydrochloric acid under certain conditions, and the salts have been assigned the following composition: $C_8H_{10}N_4O_2.HCl + 2H_2O$ and $C_8H_{10}N_4O_2.2HCl$.[1] Pure caffeine hydrochloride is however much easier obtained by simply passing dry hydrochloric acid gas into a solution of caffeine in chloroform. Washed with chloroform, and dried in an atmosphere free of moisture, it has the composition $C_8H_{10}N_4O_2.HCl$.

Compounds containing both chlorine and iodine have been reported before. Tilden[2] obtained a chloriodide of caffeine by the action of chloride of iodine upon caffeine. It combines with acids to form salts, and Tilden assigns to it the composition $C_8H_{11}N_4O_2.Cl_2I$, or $C_8H_{10}N_4O_2ICl.HCl$. But from Dittmar's[3] latest reports upon the action of chloride of iodine upon bases in general, the caffeine compound most likely has the composition as expressed by the second formula. The periodide presently to be described is however the first periodide of caffeine wherein the hydrochloric acid has the same function in the molecule as hydriodic acid usually has in the other periodides. And, to my knowledge, this is the first periodide of its kind ever reported of any base. The "periodine" in the hydrobromide is linked to the nitrogen through the bromine; in the periodides of the hydrochloride it is linked through the chlorine.

Caffeine hydrochloride diiodide is prepared by passing hydro-

[1] E. Schmidt: *Ber. d. chem. Ges.*, 14, 815.
[2] *J. Chem Soc.*, 19, 145.
[3] *Ber. d. chem. Ges.*, 18, 162.

chloric acid gas into a solution of caffeine into chloroform containing iodine. The periodide separates almost immediately in the form of compact, small, crystalline granules, of light-brown to brown color. The samples for analysis were prepared similarly to the other periodides described, and furnished the following results :

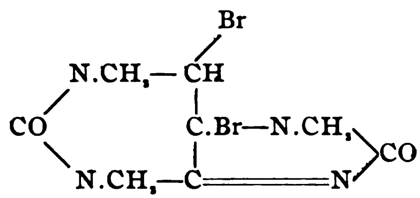
	Calculated for $C_8H_{10}N_4O_2.HCl.I_2$.	Found. I.	II.	III.	IV.	V.
I	52.34	53.38	52.44	53.44	52.88	53.64
HCl	7.53	7.40	....	....	....	....

The periodide is of a light brown color, crystalline, and melts at 165° C. Digested with excess of iodine for several days, it refuses to take up any more iodine. It is rapidly decomposed by water. Both methyl and ethyl alcohol remove the iodine readily and completely, leaving a white powder of caffeine hydrochloride. The periodide is soluble in ethyl acetate with partial decomposition, is insoluble in either cold or hot chloroform, and is not affected by ether. Exposed over potassium hydroxide in a desiccator it remains unchanged, but slowly loses iodine when exposed to air not freed from moisture. On heating to 100° C. all the iodine is driven off. Thus in all its properties it is even less stable than the periodide of caffeine hydrobromide.

III. PERBROMIDES OF CAFFEINE.

The action of bromine upon caffeine has been the subject of investigation many times. When pure bromine is employed, in absence of water, the final action of bromine results in the formation of a substitution product, bromocaffeine, $C_8H_9BrN_4O_2$.[1] In presence of water the action of bromine upon caffeine is for the most part that of an oxidizing agent, as has been shown by Maly and Hinteregger.[2] But under whatever conditions bromine is added to a solution of caffeine or to the dry base, be it as bromine-water or pure bromine, there is at first thrown down an orange-red to a brick-red precipitate. According to Maly and Hinteregger's results of analysis it is a mere addition product, caffeine dibromide, and E. Fisher[3] expresses the same opinion. The constitution of the compound is presumably this :

1 O. Schultzen : *Ztschr. Chem.*, *1867*, 614 : E. Fisher : *Ann. Chem.* (Liebig), 215, 264.
2 *Monatsh. Chem.*, 3, 85, *1882*.
3 *Ann. Chem.* (Liebig), 215, 264.



I have subjected caffeine to the action of bromine under many varied conditions, but in no case have I been able to obtain this addition product. Indeed, as will be shown, its existence is entirely hypothetical. Although Maly and Hinteregger's results of analysis agree with the theoretical figures of the formula assigned by them to the compound, yet their method of obtaining and purifying the substance for analysis is such, as to preclude the reliability of the results of analysis. The addition compound will be shown to have the composition $C_8H_{10}N_4O_2$-$HBr.Br_4$, and not $C_8H_{10}N_4O_2.Br_2$. This perbromide loses a portion of its bromide quite readily; consequently, it must be analyzed, or at least protected from exposure, as soon as dry. Hence, Maly and Hinteregger's results, obtained upon samples which have been previously exposed over lime in a desiccator for several weeks, cannot furnish reliable data as to the composition of the original substance. Just as under the action of iodine in presence of hydriodic acid, caffeine exhibits a great tendency to form higher periodides, so under the action of bromine it always forms the tetrabromide of the hydrobromide. This takes place whether hydrobromic acid be added as such or not. When none is added, some hydrobromic acid is produced, either by the action of bromine upon water or by the direct action upon caffeine,

$$C_8H_{10}N_4O_2 + Br_2 = C_8H_9BrN_4O_2 + HBr.$$

It is only under special conditions that lower perbromides of caffeine are obtained.

Caffeine Hydrobromide Tetrabromide, $C_8H_{10}N_4O_2.HBr.Br_4$.—Whenever bromine is allowed to act upon caffeine, this perbromide is one of the first products of the reaction, if not the only one. It is produced in presence or in absence of hydrobromic acid, in presence of water, of chloroform, or when pure bromine is employed.

1. *In Presence of Water.*—When bromine-water is gradually added to a solution of caffeine acidulated with hydrobromic acid, there is produced a yellow amorphous precipitate, which becomes darker, and more compact; also, if the addition of bromine be very gradual, the precipitate becomes crystalline. The same compound is however obtained easier, and more crystalline, by the following method of procedure: A stream of carbon dioxide is allowed to bubble through a column of pure bromine. and the fumes of the latter, greatly diluted with carbon dioxide, are carried into a solution of caffeine containing some hydrobromic acid. As the bromine first reaches the solution, the bubble of the gas becomes surrounded with a pale-yellow film, which soon grows darker, and the product finally settles to the bottom as an orange-red crystalline deposit, consisting of distinct small prisms. If the bromine fumes be passed into the solution too rapidly, the resulting product is amorphous. One gram of caffeine furnishes by this method two and three-tenths grams of the perbromide, which is about eighty per cent. of the theoretical value. The samples for analysis were filtered, by the use of a pump, washed with weak bromine-water, and dried by pressing on very porous plates. When dry, in about two hours, the upper layer of the mass is removed, and the rest is put away in small glass-stoppered bottles, where it remains unchanged for weeks. The washing and drying should not be prolonged any more than is necessary, as the compound loses bromine readily, especially when moist and exposed to open air. The samples were analyzed for the "exterior" bromine and for total bromine. The first was estimated by suspending a weighed quantity of the sample in a solution of potassium iodide, and the iodine thus liberated is titrated with a standard solution of sodium thiosulphate. The total bromine was estimated by precipitation with silver nitrate, in a manner entirely similar to that employed in the estimation of total iodine in the periodides. Several samples, prepared separately, gave the following results:

	Calculated for $C_8H_{10}N_4O_2.HBr.Br_4$.	Found. I.	II.	III.	IV.	V.	VI.
Total bromine	67.23	67.37	65.74	67.89	....	....	....
"Perbromine"	53.78	54.00	52.07	54.04	54.18	53.11	52.58

The addition of hydrochloric acid or sulphuric acid, instead of

the hydrobromic, does not give perbromides of salts of these acids, but the same perbromide of the hydrobromide of caffeine.

The same product is obtained even if no acid whatever be added. Thus, when fumes of bromine, absolutely free from hydrobromic acid, are passed into a solution of caffeine, there appears after a short time a precipitate of exactly the same appearance and composition as the perbromide described above. The precipitation is much slower than when hydrobromic acid is present, nor is the yield so large. One gram of caffeine yields from two-tenths to three-tenths gram of the perbromide, which is only about eight to ten per cent. of the theoretical value. Samples for analysis, prepared as previously described, gave the following figures:

	I.	II.	III.
Total bromine	65.92	....	....
"Perbromine"	52.57	53.27	54.75

This is undoubtedly the same perbromide as obtained in presence of hydrobromic acid. The slow precipitation and the small yield point conclusively that a large portion of the caffeine suffers some other changes, namely, those of oxidation and substitution, either of which would give rise to hydrobromic acid. The acid thus produced would at once tend to form the perbromide of the hydrobromide of caffeine. Filtrates from such perbromides invariably give within a short time bulky precipitates of the white bromocaffeine, $C_8H_9BrN_4O_2$.

Great precautions were taken to insure the absence of hydrobromic acid in the bromine used. For this purpose the latter was washed with a solution of sodium hydroxide, then with sulphuric acid, and finally kept under a column of sulphuric acid saturated with silver sulphate. In some experiments the fumes were also passed through a second bottle containing sulphuric acid and silver sulphate. But the perbromide of the hydrobromide was always produced even under these conditions.

Properties.—The perbromide consists of small orange-red prismatic crystals. It melts sharply at 170° C. with previous decomposition into the dibromide, and finally decomposes completely. When suspended in water, it gives up some of its bromine, and then gradually and slowly changes into the white bromocaffeine.

Two grams of the perbromide change in this way completely in about one week. When spread out on plates and exposed to air for about twenty-four hours, it loses two atoms of bromine, leaving a more stable residue, the corresponding dibromide, which suffers very little loss of bromine on further exposure. The tetrabromide is quite soluble in alcohol, more so when warm, from which it separates, on cooling, in the form of a lower perbromide mixed with some pure caffeine. Methyl alcohol dissolves the tetrabromide very readily, with the production of large quantities of formic aldehyde, and almost complete reduction of the bromine. It dissolves in warm ethyl acetate, and this on evaporation furnishes yellow crystals of a lower perbromide. The perbromide is only slightly soluble in either hot or cold chloroform. Ether removes two atoms of bromine, leaving the yellow dibromide of caffeine hydrobromide. When heated, the tetrabromide loses a portion of its bromine, and finally changes into bromocaffeine, especially at a higher temperature, about 160°–170° C.

2. *Action of Bromine in the absence of Water.*—When a weak solution of bromine in chloroform is added to a solution of dry caffeine in the same solvent, there appears after some hours' standing a deposit of flaky crystals. With strong solutions of bromine the formation of crystals begins to take place at once, the amount constantly increasing. The mother liquids, after filtering off the crystals, give new crops of the same compound. It was the compound thus produced that was analyzed by Maly and Hinteregger, after being allowed to stand several weeks over lime. The perbromide was filtered, washed with chloroform containing bromine, and dried on porous plates. It was found to be identical in composition with the one obtained similarly but with the previous addition of hydrobromic acid gas also dissolved in chloroform. The analyses I. and II. are upon samples obtained without the use of hydrobromic acid, while analyses III. and IV. are upon samples prepared with the addition of the acid.

	I.	II.	III.	IV.
Total bromine	68.25	....	....	....
Perbromine	52.25	54.79	54.40	52.82

The perbromide thus obtained is entirely identical in its behavior towards different reagents and solvents with that obtained by the action of bromine upon caffeine in presence of water. It melts at 170° C.

The question may be asked, whence comes the hydrobromic acid that furnishes the hydrobromide of the base? The bromine used in all these experiments was carefully freed from any hydrobromic acid that might have been originally present. The chloroform also was dehydrated for several days over fused calcium chloride, and finally carefully distilled. Blank experiments with absolutely dry chloroform (distilled over phosphorus pentoxide) have established that there is practically no absorption of bromine by the chloroform, when at three per cent. solution of the halogen in that liquid is exposed to light for several days. Therefore, the hydrobromic acid in the reaction could not have been produced from the substituting action of bromine upon chloroform, a reaction which takes place only at higher temperatures. From the rapid formation of the perbromide when strong solutions of bromine are used, it may reasonably be assumed that at least a portion of the hydrobromic acid, if not all of it, must have been produced directly as one of the products of the substituting action of bromine upon caffeine itself, thus:

$$C_8H_{10}N_4O_2 + Br_2 = C_8H_9BrN_4O_2 + HBr.$$

Additional proof to this theory is lent by the fact that by fractional precipitation, products are eventually obtained which give somewhat higher results for total bromine, while the "perbromine" is about the same. This would point towards the formation of $C_8H_9BrN_4O_2.HBr.Br_4$, a compound, the description of which will be given further on. The last crops of crystals show also a lower melting-point, 150°–156° C.; and when the crystals are suspended in water and treated with sulphurous acid, they yield besides caffeine an insoluble precipitate of the white bromocaffeine.

3. *Action of Pure Bromine.*—When dry caffeine is slowly added to pure bromine the first portions go into solution, but further addition produces a dark-red insoluble mass, which was supposed by Maly and Hinteregger, and by E. Fisher, to be the

caffeine dibromide, $C_8H_{10}N_4O_2.Br_2$. It is. however, not that, but the same tetrabromide of caffeine hydrobromide just described, mixed with a similar perbromide of bromocaffeine.

Dry caffeine was slowly added to a large excess of bromine free from hydrobromic acid, and the mixture was allowed to stand six hours. The thick dark mass was then spread out on porous plates, and allowed to remain over lime for three days. It was then divided into three portions: (*a*) was analyzed at once, (*b*) was washed with chloroform, and (*c*) was again redigested in pure bromine. The results of analysis are as follows:

	a.	*b.*	*c.*
Total bromine	69.45	68.50	68.03
Perbromine	53.88	54.60	53.07

On treatment with reducing agents there is left a slight residue of the insoluble bromocaffeine, and its formation would readily account for the high results of total bromine. The reaction then in this case is the same as when chloroform is employed. A small portion of the caffeine is at once attacked by the bromine and forms bromocaffeine and hydrobromic acid. The acid at once unites with the unchanged caffeine and forms the insoluble perbromide, thus protecting it against further direct action of bromine; then the bromocaffeine is in its turn slowly changed into a similar perbromide.

So far, then, as experimental evidence goes, the caffeine dibromide, $C_8H_{10}N_4O_2.Br_2$, is entirely hypothetical. It may still be said that the evidence does not exclude the possibility that only two atoms of bromine go to form the perbromide, while the other two atoms are retained by caffeine through the unsaturated lining between the two carbon atoms. Against this view there stands the simple fact that iodine, even in dilute solutions in water, forms the analogous tetraiodide. It is hardly probable that iodine would attach itself so readily to carbon. Then again, no assimilation of either bromine or iodine by caffeine takes place unless some acid be present. Hence, the constitution of this perbromide must be analogous to that of the periodide, *i. e.*, it is a pure and simple caffeine hydrobromide tetrabromide.

Caffeine Hydrobromide Dibromide, $C_8H_{10}N_4O_2.HBr.Br_2$.—When the tetrabromide is exposed to air it loses bromine, and after

twenty-four to forty hours there is left a yellow amorphous powder, which is tolerably stable and can be further exposed for many days without any appreciable loss of bromine. The results of analysis show this to be caffeine hydrobromide dibromide. The same compound is obtained by treating the tetrabromide with anhydrous ether. Samples of the tetrabromide were finely powdered under ether, and the digestion with ether was continued until fresh portions of the solvent showed no coloration when added to the perbromide. The yellow residue was filtered, washed with ether, and dried by exposure. It is identical in composition and properties with that obtained by simple exposure of the tetrabromide. Analyses I, II, and III are upon samples obtained by exposing the tetrabromide to air. Analyses IV and V are upon samples obtained by treatment with ether.

	Calculated for $C_8H_{10}N_4O_2.HBr.Br_2$.	Found. I.	II.	III.	IV.	V.
Total bromine	55.17	....	53.45	....	54.99	....
Perbromine	36.78	36.48	35.50	35.93	36.87	35.83

The dibromide ranges in color from pale-yellow to a decided yellow. It is amorphous, and melts at 170° C. When suspended in water it turns orange-red, and, as analysis shows, is changed into the tetrabromide. It is soluble in ethyl alcohol with less decomposition than the higher perbromide. On cooling the alcohol it separates in distinct tetrahedral crystals, containing less bromine than the original compound (total = 42.50 per cent., and "exterior" bromine 27.8 per cent.) Methyl alcohol dissolves the dibromide even more readily than ethyl alcohol, also with less decomposition than it does the higher perbromide. It is slightly soluble in ethyl acetate, insoluble in chloroform and ether. It remains tolerably permanent when heated to 100° C., but, on prolonged heating, or at higher temperature, it is rapidly converted into bromocaffeine.

Caffeine Hydrochloride Tetrabromide, $C_8H_{10}N_4O_2.HCl.Br_4$.—The preparation of this perbromide requires many precautions, for otherwise the product is impure, being mixed with the perbromide of the hydrobromide. First of all, the bromine must be perfectly free from hydrobromic acid, and the chloroform must be free from alcohol and moisture. Second, a dilute solu-

tion of bromine must be employed, so dilute that the addition of it to caffeine should produce no precipitation of the perbromide of caffeine hydrobromide within at least one-half hour. When all these conditions are observed, the perbromide of the hydrochloride is readily obtained by passing a stream of dry hydrochloric acid gas into a dilute solution of caffeine and bromine in chloroform. It separates in compact red crystals. The acid must be passed into the solution very slowly to prevent the formation of pure caffeine hydrochloride; care must also be taken to replace the bromine as it is gradually being used up, avoiding, however, a large excess of it at any time. The substitution of carbon tetrachloride for chloroform will not answer, for although caffeine is so readily soluble in the latter, it is almost insoluble in the former. Samples were washed with chloroform, dried in the usual manner, and analyzed for the exterior bromine and for hydrochloric acid. The latter was estimated by subtracting from the total weight of the mixed silver halides the quantity of silver bromide corresponding to the bromine as found by titration with sodium thiosulphate. The analysis furnished the following figures:

	Calculated for $C_8H_{10}N_4O_2.HCl.Br_4$.	Found. I.	II.	III.
Bromine	58.14	56.75	56.70	56.00
HCl	6.61	6.98	....	....

This compound is of a somewhat lighter color than the corresponding hydrobromide. The crystals, when examined under the microscope, present the appearance of the distinct prisms. The perbromide melts at 149° C. sharp. Suspended in water, it remains unchanged for a time, then decomposes, and finally yields bromocaffeine. Methyl and ethyl alcohol, as well as ether, convert it into caffeine hydrobromide dibromide. Exposed to air, it loses bromine more rapidly than the corresponding tetrabromide of the hydrobromide. On gentle warming for two or three days it still retains a decidedly yellow color.

IV. PERHALIDES OF CHLOROCAFFEINE.

It appears from the results which have been presented that caffeine, although a weak base, forms tolerably stable and rather high perhalides. I have next attempted to prepare perhalides

of chloro- and bromocaffeine, and compare these with those of caffeine itself. One would judge, *a priori*, that the introduction of such strong negative elements as chlorine and bromine into a weak base, would greatly weaken its tendency to form perhalides. And yet, experience shows that the halogen substitution derivatives of caffeine are still capable of forming definite salts, and that they also form even higher perhalides than caffeine itself.

Chlorocaffeine Hydriodide, $C_8H_9ClN_4O_2.HI$.—This salt can only be prepared in absence of water. Chlorocaffeine, prepared according to E. Fisher's[1] method, is dissolved in chloroform, and a stream of dry hydriodic acid gas is passed into the solution. The salt soon separates in the form of white heavy crystals. These are filtered, washed with chloroform, dried first by exposure and finally over solid potassium hydroxide. The acid was estimated by suspending a weighed quantity in water and titrating with a twentieth-normal solution of potassium hydroxide, using phenolphthalein as an indicator.

	Calculated for $C_8H_9ClN_4O_2.HI$.	Found.
HI	35.82	35.69

The salt is decomposed at once by water and alcohol. It gives up its hydriodic acid when exposed to air, probably through absorption of moisture, for when kept over potassium hydroxide for twenty hours it still contains 35.45 per cent. of hydriodic acid.

Chlorocaffeine Hydrobromide, $C_8H_9ClN_4O_2.HBr$.—This salt is prepared similarly to the hydriodide. It is, however, less stable and loses its acid more readily. Analysis gives the following figures:

	Calculated for $C_8H_9ClN_4O_2.HBr$.	Found.
HBr	26.18	26.80

Kept over potassium hydroxide for ten hours it showed only 24.80 per cent. of hydrobromic acid.

Chlorocaffeine Hydrochloride, $C_8H_9ClN_4O_2.HCl$.—This salt is still less stable than the hydrobromide. It is necessary to wash it with chloroform saturated with hydrochloric acid, and dry for analysis as rapidly as possible.

[1] *Ann. Chem.* (Liebig), 215, 262.

	Calculated for $C_8H_9ClN_4O_2.HCl$.	Found.
HCl	13.75	12.92

Kept over potassium hydroxide for 6 hours it showed only 6.15 per cent. of hydrochloric acid.

Chlorocaffeine Hydriodide Pentiodide, $C_8H_9ClN_4O_2.HI.I_5$.— Chlorocaffeine is dissolved in chloroform and is mixed with a solution of iodine in the same solvent. A slow stream of dry hydriodic acid gas is now passed into the mixture. A black amorphous powder separates at once. This is finely powdered and redigested with a fresh solution of iodine in order to insure complete reaction. If it had been previously completed, no further absorption of iodine will take place. The periodide is filtered, washed with chloroform, and dried in the usual manner. The "periodine" is estimated by titration with sodium thiosulphate. The total iodine is estimated by subtracting from the mixed silver halides (by Carius' method) the quantity of silver chloride which corresponds to the chlorine in the chlorocaffeine. The results of analysis are as follows :

	Calculated for $C_8H_9ClN_4O_2.HI.I_5$.	Found. I.	II.	III.
Total iodine	76.78	76.15	....	....
Periodine	63.99	63.08	62.66	62.75

This periodide is a black amorphous powder with a slightly bluish tint. It melts at 185°–6° C. It is decomposed by water, alcohol, more readily by methyl alcohol, by ether and ethyl acetate, giving in all cases the white chlorocaffeine. It is slightly soluble in chloroform. Washing the periodide with a large amount of chloroform does not diminish the per cent. of the halogen in the compound. When exposed to air it shows only slight signs of alteration, and even on heating the periodide at 100° C. for twenty-four hours, only a portion of the iodine can be driven off.

Chlorocaffeine Hydrobromide Pentiodide, $C_8H_9ClN_4O_2.HBr.I_5$.— This periodide is prepared by the same method as the periodide just described, substituting hydrobromic for hydriodic acid. If the acid be passed rapidly, the periodide comes down amorphous; if slowly, it assumes a crystalline appearance. Redigestion in a fresh solution of iodine shows no increase in the per cent. of

iodine in the periodide. On being washed with pure chloroform the periodide suffers no appreciable loss of the halogen. It was analyzed with the following results :

	Calculated for $C_8H_9ClN_4O_2.HBr.I_6$.	Found. I.	II.	III.
Iodine	67.15	65.5	67.07	66.29
HBr	8.49	....	8.21	....

The hydrobromic acid was estimated by subtracting from the mixed silver halides (by Carius' method) the quantities of silver chloride and iodide which correspond to the chlorine of chlorocaffeine, and to the iodine as found by titration respectively.

In appearance this periodide is not quite as black as the periodide of the hydriodide. It melts at 169° C. It is however far less stable than the hydriodide, giving up its iodine very readily to water, alcohol, ether, and ethyl acetate ; somewhat soluble in chloroform. When exposed to air it loses its iodine very rapidly, and on gentle warming leaves pure chlorocaffeine. It is even more unstable than the periodide of the hydrochloride of chlorocaffeine, an irregular gradation of stability as compared with that of the periodides of caffeine itself.

Chlorocaffeine Hydrochloride Tetraiodide, $C_8H_9ClN_4O_2.HCl.I_4$. —The preparation of this compound has been attended with some difficulties, because of its greater solubility in chloroform than the other periodides. The results of analysis by themselves would not entirely justify the formula of the compound as given, had it not been supported by the analysis of the far more stable periodide of bromocaffeine hydrochloride, which certainly has the analogous constitution. Washed with chloroform and dried, this periodide furnished upon analysis these figures :

	Calculated for $C_8H_9ClN_4O_2.HCl.I_4$.	Found. I.	II.	III.
Iodine	70.49	72.70	70.28	73.51 (?)

This periodide is of a blue-black color, and is crystalline. It melts at 137° C. It is decomposed by the different reagents similarly to the other periodides. It is however more stable than the periodide of the hydrobromide, losing iodine only very slowly on exposure to air. When gently heated it takes several hours to drive off all the iodine from a small sample of the periodide.

Chlorocaffeine Hydrobromide Pentabromide, $C_8H_9ClN_4O_2.HBr.Br_5$.—When a solution of chlorocaffeine in chloroform is treated with bromine and set aside, there appear within twenty-four hours long beautiful red crystals. The more bromine added, the quicker and more abundant is the crop; if quite a strong solution of bromine in chloroform be employed, the crystals appear within ten to fifteen minutes. On the other hand, the more carefully the bromine and chloroform are freed from traces of moisture, alcohol, and hydrobromic acid, the longer is the formation of the crystals delayed. But even with the most carefully purified reagents I have never failed to obtain them sooner or later. Several samples prepared independently were filtered, washed with chloroform containing some bromine, and rapidly dried. The total bromine was estimated by Carius' method. The analysis gave the following results:

	Calculated for $C_8H_9ClN_4O_2.HBr.Br_5$.	Found. I.	II.	III.	IV.
Total bromine	67.66	65.98	....	66.57	....
Perbromine	56.38	55.25	55.02	55.42	55.00

The results of analysis show conclusively that we have here a perbromide of a hydrobromide. To confirm this, I have prepared the same compound by passing hydrobromic acid gas into a solution of chlorocaffeine and bromine in chloroform. The perbromide, which separated as a heavy amorphous sediment, gave these figures:

Total bromine	67.04
Perbromine	55.87

Whence comes the hydrobromic acid? Some of it at least is probably produced by the action of bromine upon traces of moisture present in the reagents. It is not improbable that some hydrobromic acid results from the substituting action of bromine upon chloroform, a reaction which is extremely slow when the reagents are pure, but may be induced or facilitated by the presence of foreign bodies, like chlorocaffeine in this case. Then again, a small portion of chlorocaffeine is probably decomposed, in some way, by bromine with the production of hydrobromic acid; and this, as soon as formed, unites with the unattacked chlorocaffeine and forms the perbromide. This would

explain why, even when pure reagents are employed, the formation of crystals begins very soon after the addition of bromine, provided it be added in large excess.

The perbromide, when crystalline, consists of dark-red short thick prisms. It melts at 151° C. It is decomposed by water, alcohol, ethyl acetate, giving a residue of pure chlorocaffeine. It is insoluble in chloroform. Ether removes only four-fifths of the "exterior" bromide, and gives a lower perbromide. Exposed to air it loses bromine quite readily, and if the exposure be prolonged, it loses all its bromine. Gentle heating greatly hastens the liberation of bromine.

Chlorocaffeine Hydrobromide Monobromide, $C_8H_9ClN_4O_2,HBr.Br$.—When the pentabromide of chlorocaffeine, finely powdered, is digested with anhydrous ether for several days, it gives up four-fifths of its "exterior" bromine. The reaction is slow towards the end and care must be taken to replace the ether with fresh portions of the solvent. The yellow residue is filtered off, washed with ether and rapidly dried. Several samples were analyzed with the following results :

	Calculated for $C_8H_9ClN_4O_2.HBr.Br$.	Found. I.	II.	III.
Total bromine	41.08	42.34	....	....
Perbromine	20.54	22.11	20.89	20.04

It is a yellow amorphous powder, of a darker shade than the corresponding derivative of bromocaffeine. It melts at 189° C., being previously decomposed into chlorocaffeine and bromine. It resembles the pentabromide in most of its properties, but seems to be somewhat more stable toward methyl and ethyl alcohol.

Chlorocaffeine Hydrochloride Pentabromide, $C_8H_9ClN_4O_2.HCl.Br_4$.—Chlorocaffeine is dissolved in dry chloroform containing bromine free from hydrobromic acid. A slow stream of dry hydrochloric acid gas is now passed into the solution. Beautiful well defined crystals soon separate. These are filtered, washed with chloroform containing bromine, and rapidly dried. Several samples gave the following results upon analysis :

	Calculated for $C_8H_9ClN_4O_2.HCl.Br_5$.	Found. I.	II.	III.
Br	60.17	58.88	57.62	58.50
HCl	5.48	5.61	....	....

The crystals, small prisms, are of a red to a scarlet-red color. The perbromide melts at 153° C. It is decomposed by water, alcohol, and ethyl acetate in about the same degree as the perbromide of the hydrobromide. On exposure to air, or on gentle heating, it does not seem to lose bromine any faster than the perbromide of the chlorocaffeine hydrobromide.

V. PERHALIDES OF BROMOCAFFEINE.

Bromocaffeine, like the chloro compound, is capable of forming salts and perhalides, provided the proper conditions are observed. In general, the salts are even more stable than those obtained from chlorocaffeine; this is also true, in general terms, of the perhalides.

Bromocaffeine[1] *Hydriodide*, $C_8H_9BrN_4O_2.HI$.—Prepared and analyzed like the corresponding salt of chlorocaffeine, it furnished these figures:

	Calculated for $C_8H_9BrN_4O_2.HI$.	Found. I.	II.	III.
HI	31.83	31.49	32.18	32.52

Kept over potassium hydroxide for two days it showed no loss of hydriodic acid.

Bromocaffeine Hydrobromide, $C_8H_9BrN_4O_2.HBr$.—This salt has to be washed with chloroform saturated with hydrobromic acid, for otherwise it dissociates and gives upon analysis low results:

	Calculated for $C_8H_9BrN_4O_2.HBr$.	Found. I.	II.	III.
HBr	22.89	21.22	19.00	23.50

The salt is tolerably stable when protected from moisture.

Bromocaffeine Hydrochloride, $C_8H_9BrN_4O_2.HCl$.—Prepared in the same manner as the other salts, it furnished the following results:

	Calculated for $C_8H_9BrN_4O_2.HCl$.	Found. I.	II.
HCl	11.77	11.79	11.43

This salt is far more stable than the hydrochloride of chlorocaffeine. Left over potassium hydroxide for twenty hours, it lost only 0.70 per cent. of hydrochloric acid.

Bromocaffeine Hydriodide Pentiodide, $C_8H_9BrN_4O_2.HI.I_4$.—This periodide has been prepared similarly to the analogous

[1] Prepared according to E. Fisher's method, *Ann. Chem.* (Liebig), 215, 264.

periodide of chlorocaffeine. Washed with chloroform, dried and analyzed, it gave the following results, as obtained upon separate samples :

	Calculated for $C_8H_9BrN_4O_2.HI.I_4$.	Found. I.	II.	III.
Total iodine	74.32	72.86	....	....
Periodine	61.22	60.52	60.22	61.27

It is a dull-black amorphous powder, melting at 183° C. It is decomposed by water, alcohol, ether, and ethyl acetate, but slower than the analogous periodide of chlorocaffeine. It is insoluble in chloroform. The sample that furnished analysis I. was boiled for some time with chloroform, and still gave upon titration with sodium thiosulphate 60.39 per cent. of iodine. It loses iodine very slowly on exposure, and even on warming, the liberation of iodine is slow.

Bromocaffeine Hydrobromide Pentiodide, $C_8H_9BrN_4O_2.HBr.I_4$. —This periodide forms very slowly, and the product, as first obtained, must be redigested in fresh solutions of iodine in chloroform, in order to insure a uniform and constant sample. When all the salt has been thus converted into the pentiodide, further digestion with iodine does not give any higher periodide ; and when the pentiodide is washed with large quantities of pure chloroform, it loses none of its " exterior" iodine. Several samples were analyzed with the following results :

	Calculated for $C_8H_9BrN_4O_2.HBr.I_4$.	Found. I.	II.	III.
I	64.12	65.40	63.88	64.53
HBr	8.12	....	8.42	....

This periodide is amorphous, of a dark-brown color, and melts at 160° C. It is decomposed by the different reagents like the similar periodide of chlorocaffeine. Unlike the latter, it loses iodine only very slowly on exposure, but quite rapidly when warmed. In this respect, then, it is a more stable compound than its analogue of chlorocaffeine.

Bromocaffeine Hydrochloride Tetraiodide, $C_8H_9BrN_4O_2.HCl.I_4$. —Just as the hydrochloride salt of bromocaffeine is more stable than the hydrochloride of chlorocaffeine, so is the periodide of the former easier obtained in pure state than that of the latter. When hydrochloric acid gas is passed into a solution of bromo-

caffeine and iodine in chloroform, the periodide comes down at once pure, either in brown or dark-blue crystals, depending upon the rate with which the hydrochloric acid is passed into the solution. Samples were washed with chloroform containing hydrochloric acid, dried and analyzed with the following results :

	Calculated for $C_8H_9HBrN_4O_2.HCl.I_4$.	Found. I.	II.	III.
I	62.06	61.50	60.53	61.14
HCl	4.46	4.27	....	....

Bromocaffeine, then, agrees with chlorocaffeine in that respect that they both form *tetraiodides* of their respective hydrochlorides. The periodide of bromocaffeine hydrochloride is much less stable than the periodide of the hydrobromide, and in this respect bromocaffeine differs from chlorocaffeine, for in the latter the gradation of the stability is in the reverse order. This periodide consists of well-defined brown or dark-blue crystals, melting at 136° C. It is readily decomposed by the various reagents. Exposed to air, it loses nearly all its iodine in a comparatively short time, and still more rapidly when warmed.

Bromocaffeine Hydrobromide Pentabromide, $C_8H_9BrN_4O_2.HBr.Br_4$.—All that has been said about the formation of the perbromide of chlorocaffeine applies equally well in the case of bromocaffeine. A solution of the latter in chloroform containing bromine begins to deposit long slender crystals within five to six hours, and the crop gradually increases as the solution is allowed to stand. Even when the reagents employed are carefully freed from traces of moisture and hydrobromic acid, the formation of the perbromide still takes place, being more rapid as the amount of bromine added is increased. The perbromide, thus obtained, is entirely identical with the one which is formed when dry hydrobromic acid gas is passed into a solution of bromocaffeine and bromine in chloroform, except that in the latter case the product is amorphous. All that has been said about the possible sources of the hydrobromic acid in the case of the perbromide of chlorocaffeine, must apply fully as well to the perbromide of bromocaffeine. Uufortunately, neither of the two halogen substitution products of caffeine are soluble in carbon tetrachloride, and therefore the latter could not be used instead of

chloroform. The total bromine was found by subtracting from the total silver bromide, as obtained by Carius' method, that amount of it which corresponds to the bromine in bromocaffeine proper. The results of the analysis of several samples are as follows:

	Calculated for $C_8H_9BrN_4O_2.HBr.Br_4$.	Found. I.	II.	III.	IV.	V.
Total bromine......	63.68	64.17	....	64.31	....	64.53
Perbromine........	53.05	54.15	53.23	53.40	53.25	53.65

Analyses I, II, III and IV are upon samples prepared without the addition of hydrobromic acid, while Analysis V is upon a sample obtained with addition of the acid.

This perbromide consists of short prisms of a dark orange-red color, melting at 156° C. It resembles in general behavior the analogous perbromide of chlorocaffeine. It is decomposed by the various reagents, and on exposure loses all its bromine. When treated with ether it, too, forms the lower perbromide.

It may be said, that whatever the case be with pure caffeine itself, the perbromides of the halogen substitution derivatives of the base may after all have two bromine atoms linked to the unsaturated carbon atoms, and only the three remaining bromine atoms form the true perbromide. That is, the constitution of the perbromides should be represented by Formula I, and not by II.

I.

$$
\begin{array}{l}
\qquad\quad\;\; Br \\
CH_3.N—CX \\
\qquad \dot{C}O\ \dot{C}Br.N.CH_3 \\
CH_3.N—C:N{>}CO\ ,(HBr.Br_2).
\end{array}
$$

II.

$$
\begin{array}{l}
CH_3.N—CX \\
\qquad \dot{C}O\ \ddot{C}.N.CH_3 \\
CH_3N—C:N{>}CO\ ,(HBr.Br_4).
\end{array}
$$

In favor of this view, we have the fact that the introduction of a negative group (X) into the caffeine molecule favors the formation of such additive products. Thus, E. Fisher[1] has found

[1] *Ann. Chem.* (Liebig). 215, 272.

that hydroxycaffeine readily unites with bromine, and the resulting additive product has not unlikely this composition : $C_8H_9(OH)N_4O_2.Br_2$. But against this view we have (1) that no such dibromo-additive compounds of either chloro or bromocaffeine has ever been isolated ; (2) that even iodine makes the penta-perhalides, and not the tri-perhalides, as we should otherwise expect, and (3) that the formation of the perhalides of bromo and chlorocaffeine takes place only in presence of some halogen acid.

Bromocaffeine Hydrobromide Monobromide, $C_8H_9BrN_4O_2HBr.Br$.—This is formed when the higher perbromide is treated with anhydrous ether until fresh portions of the latter are no longer colored by the perbromine. Washed with ether and dried, several independent samples were analyzed with the following results :

	Calculated for $C_8H_9BrN_4O_2.HBr.Br$.	Found. I.	II.	III.
Total bromine	36.86	37.35	....	....
Perbromine	18.43	18.68	20.39	20.04

This perbromide is of a lighter yellow color than the corresponding perbromide of chlorocaffeine ; in all other respects the two compounds apparently agree. It melts at 206° C., suffering, previously to melting, decomposition into bromocaffeine, hydrobromic acid, and bromine.

Bromocaffeine Hydrochloride Pentabromide, $C_8H_9BrN_4O_2.HCl.Br_4$.—Bromocaffeine is dissolved in chloroform, bromine free from hydrobromic acid is added, and a slow stream of hydrochloric acid gas is now passed into the mixture. The separation of the perbromide begins to take place at once, in the form of deep-red needle-like crystals. Samples thus prepared were analyzed with the following results :

	Calculated for $C_8H_9BrN_4O_2.HCl.Br_4$.	Found. I.	II.
Br	56.40	55.25	55.18
HCl	5.13	5.02	....

This perbromide resembles very closely the perbromide of the hydrobromide, but it seems to give off bromine more readily than the latter. It melts at 157° C. It is decomposed by the various reagents, and gives pure bromocaffeine.

VI. SUMMARY.

The results described in the preceding pages are presented in a condensed form in the subjoined table. In general terms, the perhalides, as given in the table, decrease in stability as we read from left to right. For example, of the periodides of the hydriodides, that of caffeine is the most stable, next comes that of bromocaffeine, and this is followed by the one of chlorocaffeine. The same is true of the periodides and perbromides of the other salts. While the line is quite sharp between the perhalides of caffeine and those of bromocaffeine, it is not so between the perhalides of the latter and those of chlorocaffeine. We can speak only in general terms of a difference in stability between the perhalides of the two halogen caffeines, respectively. Thus, we notice such a difference in stability between the periodides of the two hydrobromides, and also between the perbromides of the two hydrochlorides respectively. The gradation in stability among the periodides of one and the same class is usually, but not always, regular. In all three cases, however, the periodides of the hydriodides are far more stable than those of the other salts. If *a*, *b*, and *c* should represent different degrees of stability, decreasing in alphabetical order, then the *relative* stability of the members of each class of the perhalides is as is given in the table. It must be understood that the term *stability* is used here in its broad and general sense, such as the behavior of the compounds towards different solvents, and on exposure to air. The comparison is made between the perhalides of each class, and periodides, as well as the perbromides of each of the three bases (caffeine, bromocaffeine, and chlorocaffeine) form separate classes for comparison. When two perhalides of the same salt exist, only the higher one is taken into account.

There appears to be a regular lowering in the melting-points of the periodides of each class, it being the highest in the hydriodides and the lowest in the hydrochlorides. It is a curious coincidence that the melting-points of the analogous periodides of chlorocaffeine and bromocaffeine are so near alike, while the pure halogen caffeines themselves melt at 188° C. and 206° C., respectively. The perbromides do not show such a regular gradation. There is a difference in stability of the periodides of each class, corresponding to the lowering of the

	Acid combined with base.	Caffeine. Perhalides.	Stability.	M. P.	Bromocaffeine. Perhalide.	Stability.	M. P.	Chlorocaffeine. Perhalide.	Stability.	M. P.
Periodides.	HI.	$C_8H_{10}N_4O_2.HI.I_2$		171°						
	HI.	$C_8H_{10}N_4O_2.HI.I_4$	*a*	215°	$C_8H_9BrN_4O_2.HI.I_4$	*a*	183°	$C_8H_9ClN_4O_2.HI.I_5$	*a*	185°
	HBr.	$C_8H_{10}N_4O_2.HBr.I_5$	*b*	183°	$C_8H_9BrN_4O_2.HBr.I_5$	*b*	160°	$C_8H_9ClN_4O_2.HBr.I_5$	*c*	169°
	HCl.	$C_8H_{10}N_4O_2.HCl.I_2$	*c*	165°	$C_8H_9BrN_4O_2.HCl.I_4$	*c*	183°	$C_8H_9ClN_4O_2.HCl.I_4$	*b*	137°
Perbromides.	HBr.	$C_8H_{10}N_4O_2.HBr.Br_2$		170°	$C_8H_9BrN_4O_2.HBr.Br.$		206°	$C_8H_9ClN_4O_2.HBr.Br$		189°
	HBr.	$C_8H_{10}N_4O_2.HBr.Br_4$	*a*	170°	$C_8H_9BrN_4O_2.HBr.Br_5$	*a*	156°	$C_8H_9ClN_4O_2.HBr.Br_5$	*a*	151°
	HCl.	$C_8N_{10}N_4O_2.HCl.Br_4$	*b*	149°	$C_8H_9BrN_4O_2.HCl.Br_5$	*b*	157°	$C_8H_9ClN_4O_2,HCl.Br_5$	*b*	153°

melting-points, this being true of caffeine and bromocaffeine, where the periodide of the hydrobromide is less stable than the hydrochloride. There is a uniformity in composition between the periodides on one hand and the corresponding perbromides on the other, in each of the three bases. Thus, in caffeine it is always the tetrahalide compound that is more easily formed, and in chlorocaffeine and bromocaffeine it is the pentahalide. It will be noticed that all three hydrochlorides carry less iodine in the periodides than the salts of the other two halogen acids.

It is difficult to draw very general conclusions from the study of perhalides of only one base, but so far as they go, the results presented in the preceding pages justify in a certain degree the following conclusions:

(1) Organic bases are capable of forming periodides not only of their hydriodide salts, but also of the hydrobromides and of the hydrochlorides. The stability of the resulting periodide will be governed, all other conditions being equal, by the nature of the halogen through which the "periodine" is linked to the nitrogen, decreasing as the volatility of the halogen increases.

(2) When a base forms periodides, it is also capable of forming perbromides, which probably possess an analogous composition and constitution.

(3) If two nearly related compounds form under similar conditions periodides (or perbromides) of different degrees, then the periodide (or perbromide) containing the highest number of "perhalogen" atoms is not necessarily the more stable of the two. Compare, for instance, the tetraiodide and tetrabromide of caffeine with the pentiodide and pentabromide of bromocaffeine.

(4) The number of iodine atoms which a base takes up in the formation of a periodide is in no way an index of the basal power of the base. Caffeine, for instance, is a very weak base, yet it forms higher periodides than the comparatively stronger bases of morphine, strychnine, atropine, etc. Again, chlorocaffeine and bromocaffeine, although far weaker than caffeine itself, forms higher periodides than the latter.

In conclusion, I wish to express my thanks to Mr. J. A. Keating and Mr. W. J. O'Brien, who have kindly helped me in this work.

ANN ARBOR, MICHIGAN.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 17.]

DETERMINATION OF THE HEAT OF BROMINATION IN OILS.[1]

BY H. W. WILEY.

Received January 3, 1896.

THE qualitative value of the degree of heat produced in mixing oils with sulphuric acid, is pointed out in Bulletin No. 13, Part IV, pages 475 *et seq*. In that bulletin a great number of examples are given, showing the different behavior of different fats and oils when treated according to the method first proposed by Maumené with sulphuric acid under standard conditions. It is evident that in a process of this kind the actual rise of temperature observed is dependent upon many varying conditions, such as the initial temperature, strength of sulphuric acid, relative proportions of sulphuric acid and oil employed, perfectness of insulation and other data depending on the analytical system itself. The data obtained under standard conditions, however, are extremely valuable in discriminating between fats of different characters. For instance, the rise of temperature produced by a given weight of butter fat is only about one-fourth of that produced by an equal weight of cotton oil under the same conditions. In the bulletin mentioned above, formulas are also given whereby some quantitative idea may be obtained of the relative proportions of the two constituents in a mixed oil. The fact that the natural glycerides contain unsaturated radicals capable of combining with the halogens has long been recognized, and Hübl, as is well known, has based a quantitative method of great value upon the ability of glycerides to absorb iodine. Chlorine and bromine are also absorbed with equal or greater avidity, and attempts have been made to establish quantitative methods in which these halogens take the place of iodine in the Hübl process.

Hehner and Mitchell[2] propose an innovation upon the general principles of the Hübl method in which the degree of chemical action is not measured by the residue of the halogen left unabsorbed, but by the degree of heat produced by the chemical reaction which takes place. They have not made any attempt

[1] Read at the Cleveland Meeting, December 31, 1895.
[2] Analyst, 20, 146.

to determine the total quantity of heat by calorimetric measurement, but simply estimate the total rise of temperature produced by the reaction. This method I have subjected to a thorough analytical test, and am convinced that it has great value in

analytical operations. On account of the difficulty of executing the method as described by the authors, I have made a number of changes therein which render it not only more accurate, but, especially, more easy of application. The difficulty of handling liquid bromine in quantities of one cc. is evident to every

analyst. It is almost impossible to measure and deliver exactly this quantity of liquid bromine into the tube in which the reaction takes place. I have therefore made use of the bromine previously dissolved in chloroform or carbon tetrachloride. I find that one part by volume of bromine in four parts by volume of chloroform makes a solution which is easily kept and easily measured. To avoid any disturbing action of the bromine upon the chloroform, due to the generation of hydrobromic acid, the solution should be kept shielded from the light and only small quantities, such as may be used during the day, made up at a time. Another convenient modification has been introduced in dissolving the fats or oils in chloroform or carbon tetrachloride before beginning the analytical operations. By this means triplicate determinations, or a greater number may be made on the same sample without the trouble and annoyance of weighing each one. Ten grams of the oil or fat are dissolved in chloroform and the volume made up to fifty cc. With this volume nine determinations can easily be made, and it is recommended that at least four be made with every sample.

The apparatus employed is shown in the illustration. The tube holding the reagent and thermometer is about forty centimeters in length and one and a half in internal diameter. It is conveniently held in a drying jar, into which it fits air-tight by means of a rubber stopper. In order to secure the insulation of the inner tube, the air is withdrawn from the drying cylinder through the side tubulure. The solution of bromine and chloroform is placed in a heavy Erlenmeyer flask with a side tubulure near the top, to which is attached a rubber bulb. The flask carries a pipette held in place by a stopper, which by gentle pressure is made air-tight. The thermometer used is graduated in fifths of degrees and is easily read to tenths by means of a small magnifying glass.

The operation should be conducted in a room which is kept at as nearly as possible constant temperature during the progress of the work.

The solutions having all been prepared, they are placed upon the table with the apparatus and the whole system is allowed to stand until a constant temperature through all parts is reached.

Five cc. of the solution of the fat or oil are placed in the inner tube by means of a pipette, with care to prevent the solution coming in contact with the walls of the tube. The thermometer having been inserted, the bromine solution is forced into the pipette by compressing the rubber bulb with the left hand until the liquid has passed the mark on the stem of the pipette. The top of the pipette is now closed by the forefinger of the right hand, the pressure on the rubber bulb released, the stopper in the Erlenmeyer flask loosened and the bromine in the pipette allowed to flow out until the mark is reached. The bromine solution is transferred to the observation tube and allowed to flow directly into the solution of the fat. It is not important, in this case, to prevent the liquid from touching the sides of the tube as it enters. As soon as the pipette is empty it is withdrawn, replaced in the Erlenmeyer flask and the thermometer at once observed by means of the magnifying glass. The bromination of the fat is practically instantaneous and the mercury in the thermometer will reach its maximum height in about a minute after the pipette delivering the bromine solution is withdrawn. The whole operation of determining the heat of bromination after all the preparations are made can be accomplished within two minutes. When the mercurial column in the thermometer begins to descend, air is admitted into the outer cylinder through the stop-cock shown, the tube containing the residue of the reaction is withdrawn by loosening the rubber stopper and its contents emptied. By holding the tube with the mouth down the residual bromine vapor soon escapes and the tube may be cleaned by simply wiping it with a long test-tube cleaner, or may be used again without cleaning afteral lowing it to stand for half an hour mouth down. Any traces of brominated oil which remain upon the sides of the tube do not unfit it for subsequent use, unless thick enough to obscure the reading of the temperature. By allowing the air thus to reenter the jacket space the thermometer is soon restored to normal, and a second determination may be made within half an hour. In this way two determinations an hour can be made with the same system.

In regard to the relation which the rise of temperature, due to

bromination, has to the iodine absorption number of a fat, it is stated by Hehner and Mitchell that it is represented by the factor 5.5. It is evident, however, that this factor must be determined separately for every system of apparatus and every solvent employed. Naturally it would be different from the number stated when determined in the manner indicted above. Each analytical system, therefore, must be separately standardized, and the factor thus obtained can be used with considerable certainty for calculating the number representing the iodine absorption.

It may be mentioned that it is important not to stir or churn the mixture of the oil and bromine further than is secured by the introduction of the bromine solution itself. By a vigorous churning of the mixture, throwing the warm liquid against the cold side of the containing tube, I found it possible to reduce the rise of temperature in one instance from 19° to less than 15°. It is evident that much more accurate results could be obtained in all cases by a careful calorimetric measurement of the heat produced by the reaction. For strictly scientific purposes, this is the only rational method of procedure, but the desired end will be served equally well by carefully conducting the process in some such way as indicated above and determining for each system of apparatus employed the factor for calculating the iodine number.

Experience has shown that carbon tetrachloride, by reason of its higher boiling-point and stability, is a more convenient solvent in the preparation of the reagents than chloroform. The rise of temperature obtained, however, with solutions in carbon tetrachloride, is slightly less than in chloroform. This is not due to a higher specific heat of the carbon tetrachloride, since at 30° the specific heats of the solvents are 0.207 and 0.233 for carbon tetrachloride and chloroform respectively. Either the action of the bromine is more vigorous in the chloroform solution or else the heat due to the bromination of the chloroform and the production of hydrobromic acid is sufficient to account for the difference. In other words, we have here to deal not only with the heat of bromination of the oil, but also with that due to the formation of $CBrCl_3$ and of hydrobromic acid. This is an addi-

tional reason for preferring carbon tetrachloride as a solvent.

This action is indicated by the following data: One part of bromine and four of chloroform were placed in separate contiguous vessels, in a room subject only to slow changes of temperature, and left at rest for nineteen hours. The temperature of the two liquids at the expiration of this time was exactly 12°. On placing the thermometer in the bromine and pouring the chloroform upon it there was at first a depression of the temperature amounting to seven-tenths of a degree. In a few seconds the temperature began to rise, and at the end of three minutes it had reached 13.3°, showing a rise of over one degree above that of the original solutions.

In the following table the data representing the means of several observations in each instance are given, showing the results of the determination of the heat of bromination of four oils dissolved in the one instance in chloroform and the other in carbon tetrachloride:

Name of oil.	Solvents.	Initial temperature.	Final temperature.	Rise of temperature.
Olive oil	Chloroform	22.7°	42.2°	19.5°
Olive oil	Carbon tetrachloride	15.1	33.3	18.2
Calycanthus seed oil	Chloroform	17.2	45.9	28.7
Calycanthus seed oil	Carbon tetrachloride	19.3	47.0	27.7
Salad oil (cotton seed?)	Chloroform	17.9	43.7	25.8
Salad oil (cotton seed?)	Carbon tetrachloride	19.8	44.7	24.9
Sunflower seed oil	Chloroform	15.0	43.4	28.4
Sunflower seed oil	Carbon tetrachloride	14.0	41.6	27.6

My thanks are due to Mr. E. E. Ewell for assistance in the analytical work.

DISCUSSION.

Dr. C. B. Dudley: The detection of adulterations in commercial oils is a subject that has given us an immense amount of study in the laboratory at Altoona. The commercial results may be easily imagined when it is known that at one time during the past eighteen years lard oil was worth $1.10 a gallon, and cottonseed oil fifty cents a gallon, and that it was no uncommon practice to put into a gallon of lard oil as high as twenty-five per cent. of cottonseed oil. I should state that lard oil is used in making burning oil for hand lanterns and is commonly called signal oil. On this oil depends largely the safety of the running of

trains. Cottonseed oil being, as you all know, a semi-drying oil, and does not burn well, hence the seriousness of adulteration may be readily understood. Signal oil mixed with cottonseed oil will go out in from six to eight hours after it is lighted, at least after the first two or three times burning of a wick. The switches must be lighted fourteen hours continuously to insure safety, and the hand lanterns for signalling must be reliable. No small amount of the work done at Altoona has been done in connection with adulterations in oils. We have kept pace with every modification that would enable us to detect adulteration, and have found Maumené's test of very great value, because of its simplicity, its rapidity of application, and the constancy of the results obtained.

There are two serious defects, however, in all the tests that I have ever seen proposed for detecting adulterations in oils. These are: First, none of the proposed methods are based on any characteristic reactions of any given oil so that although we may be able to say that a sample of oil submitted to us is not pure, we are unable to say what other oil it is adulterated with. The second defect is that owing to this lack of characteristic reactions and to the peculiarities of the proposed method, mixtures of various oils can be made, which mixtures will give the same results under the tests as a pure sample of another oil. For example, it is quite easy to make such a mixture of olive and cottonseed oils that the rise in temperature obtained by Maumené's test will be the same as is characteristic of pure lard oil. And the same may be said of the iodine test, etc. So far as our knowledge goes we still lack a means of identifying the characteristic oil that may be present as an adulterant in another, and also we still lack an absolute means of saying positively that a sample of an oil is not a pure one.

SÄRNSTRÖM'S METHOD OF DETERMINING MANGANESE IN IRON ORES.

By C. T. Mixer and H. W. DuBois.

Received February 25, 1896.

ABOUT a year ago we had occasion to use a volumetric method which would allow the determination of manganese in iron ores ranging in amounts up to fifteen per cent. and give results in half an hour which would check with gravimetric determinations within two-tenths per cent. for ores as high as fifteen per cent., and within a few hundredths of a per cent. for ores under one per cent.

We found in use in a neighboring laboratory a method which was generally known as the "Swedish Method." This method was found to fulfil the above conditions, and seems to have sufficient merit to be more widely known.

The first suggestion upon which the method is based was made by Guyard,[1] although his method of operating it did not give very satisfactory results.

The first description of the method in its present practicable form, was made by C. G. Särnström, in the Jernkontorets Annaler, (Sweden), 1881, p. 401.[2]

The principle upon which this method depends, is the reaction which takes place when a manganese compound higher in oxygen than the manganous state, is dissolved in hydrochloric acid, forming a higher chloride, which is readily shown by the dark colored solution. When the solution is boiled, it rapidly decolorizes, being completely converted into manganous chloride, not easily oxidized by the air while in the acid solution.

In neutral or alkaline solutions the manganous compound has a slight tendency to oxidize in contact with the air, but we have never detected any appreciable oxidation under the conditions which we follow.

The separation of the iron and the manganese is effected in

[1] Guyard: *Chem. News*, 8, 292; the following references relate to the subsequent modifications of the method; Habich: *Ztschr. anal. Chem.*, 3, 474; Winkler: *Ztschr. anal. Chem.*, 3, 423. Morawski und Stingl: *J. prakt. Chem.* (N. F.), 18, 96; Volhard: *Ann. Chem.* (Liebig), 198, 318.

[2] Also published in Berg und Hüttenm. *Zeitung*, 40, 425. A review of the original article appears in the *Ztschr. anal. Chem.*, 22, 84. We are indebted to Mr. Hugo Carlsson, Chief Chemist of the Johnson Works of Lorain, Ohio, for calling our attention to Särnström's original publication and for furnishing us a translation of the same.

such a way that the iron is precipitated as hydroxide and the manganese left in the manganous condition in solution. Sodium carbonate is used to precipitate the iron as hydroxide and no trouble is experienced in the precipitation of the manganese as a carbonate, provided that only a very slight excess is employed beyond that necessary to completely precipitate the iron.. It is advisable to add the sodium carbonate in the form of a solution, towards the completion of the precipitation of the iron, to avoid such an excess.

Särnström employs sodium bicarbonate, which has the advantage that a greater amount of carbon dioxide is generated, preventing subsequent oxidation of the manganous salt by the oxygen in the air. Manganese bicarbonate is formed, which is readily soluble in the solution containing carbon dioxide.

It is always desirable to test the sodium carbonate or bicarbonate for organic matter.

The results given below show the necessity of avoiding an excess of sodium carbonate (the same is true of the bicarbonate) in the precipitation of the iron. Aliquot portions of a solution of manganese containing 3.14 per cent. manganese gravimetrically determined, gave only 2.61 per cent. when treated with such an excess. Another one giving 8.69 per cent. under the proper conditions of this method, when treated with an excess of sodium carbonate, gave 5.38 per cent.

After the precipitation of the iron in the hot solution, the manganese, being in the manganous state, is oxidized by potassium permanganate, according to the following formula,

$$3MnO + 2KMnO_4 + H_2O = 2KOH + 5MnO_2,$$

which is the same reaction which takes place in Volhard's method. As the titration takes place directly, without filtering, the precipitate of ferric hydroxide is an advantage, especially in low manganese ores, as it serves to collect the fine precipitate of manganese dioxide and causes it to settle more rapidly.

In ores very low in iron, it is desirable to add ferric chloride in order to obtain the requisite amount of the iron precipitate.

The Method.—Weigh half a gram ore into a No. 0 beaker, add fifteen cc. of hydrochloric acid 1.1 sp. gr., and boil until

the residue is clear. If necessary fuse the residue with sodium carbonate. Add a few drops of nitric acid to oxidize any ferrous iron or organic matter. In magnetic ores more of course will be necessary. It is well to test for ferrous iron. Evaporate a short time to expel any nitrous acid that may have been formed. It is advisable to have a good amount of free hydrochloric acid present to generate carbon dioxide in the precipitation with sodium carbonate. The solution is then washed into a No. 3 beaker or flask, which is then filled about two-thirds full with boiling, distilled water and solid sodium carbonate or bicarbonate added until the iron is completely precipitated, which is readily indicated by the characteristic spongy appearance of the precipitated ferric hydroxide. A solution of the salt is preferable for the final precipitation in order to avoid an excess.

The solution should be about 80° C. when it is titrated[1] with potassium permanganate directly, without filtering, and with intervals of vigorous stirring and settling of the iron and manganese precipitates, until the supernatant liquid shows a permanent faint pink color. The first appearance of the pink color must not be taken as an indication that the oxidation is complete, as gentle heating and vigorous stirring will allow more potassium permanganate to be added before the permanent pink appears.[2]

Multiplying the burette reading by two represents the equivalent for one gram, and this multiplied by the permanganate value in manganese, which is the iron value multiplied by 0.2946, gives the percentage of manganese.

In case of over-titration, it is practicable to titrate back with a carefully standardized solution of manganous chloride, which is prepared by evaporating fifteen cc. potassium permanganate down to three or four cc., adding a few drops of hydrochloric acid and boiling as long as chlorine comes off. The solution should be neutralized with sodium carbonate and diluted to ten cc., when one cc. is equal to one cc. of potassium permanganate.

Särnström states that the method is reliable for high manga-

[1] Which should be done immediately after the neutralization, in order to avoid any opportunity for oxidation.

[2] This is a very important point not only in relation to this method, but in all methods where potassium permanganate is used.

nese ores and ferro-manganese "where it is not necessary to determine the manganese closer than a few tenths of one per cent."

Our experience does not confirm this. The results average from one to two per cent. too low, so that we do not consider the method at all reliable for high percentages of manganese.

The following are some results which show this:

	Särnström. Per cent.	Gravimetric (Ford's) Per cent.
Illinois Ore	52.06 (1)	52.98
	51.91 (2)	....
	51.40 (3)	....
	51.78 (4)	...
	51.37 (5)	....
	51.37 (6)	....
No. 595	42.07	....
	42.35	44.3
	42.90	....
	42.60	....

In analyses from No. 1 to No. 4 sodium carbonate was used for the precipitation. To determine whether the employment of sodium bicarbonate would be advantageous, No. 6 was so treated while at the same time No. 5 was precipitated with sodium carbonate, yielding the same result. We have tried sodium bicarbonate with low manganese ores, but have never noticed any practical advantages, while theoretically, as we have pointed out above, there should be an advantage in the employment of sodium bicarbonate.

This discrepancy with high percentages of manganese may possibly be accounted for, by the fact that the large precipitate of manganese dioxide may act in a purely mechanical way in protecting the final amounts of the manganous chloride from being fully oxidized to dioxide by the potassium permanganate. It is to be noted in this connection that Volhard's method does not generally give reliable results with such high percentages of manganese.

The following are some results obtained by this and other methods:

	Särnström.	Volhard.	Gravimetric.
A. Magnetic	0.07	0.10	0.07
Specular	...	0.08[1]	...
B. Mixture of blue granular and red hematite.	0.30	0.31	0.29
	0.32	0.29	0.30
	0.28	...	...
C. Limonite	1.03	1.02	1.09
	1.05	1.05	...
D. Silicious ore	2.98	3.08	2.93
	3.07	3.07	...
Cary Empire	3.93	T. V. Church	3.94
	3.88	Illinois Steel Co	
	6.04	...	...
Dexter No. 2	6.02	6.02	6.01
	6.01	...	...
Davis ore	8.78	8.62	8.86
		A. G. McKenna,	(Ford's)
Newark ore	1.48	Duquesne Steel Works,	1.50
No. 57	5.39	5.39	...
No. 218	5.59	5.59	...

In the determination of small amounts of manganese this method presents an advantage over Volhard's method in giving a more distinct end reaction.

The method can be used for iron and steel determinations if the usual precautions are taken to oxidize the carbon. But it is not so well adopted to these on account of the impracticability of taking large amounts for analysis.

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ON VARIOUS MODIFICATIONS OF THE PEMBERTON VOLUMETRIC METHOD FOR DETERMINING PHOSPHORIC ACID IN COMMERCIAL FERTILIZERS.

BY F. P. VEITCH.

Received February 18, 1896.

If an excuse is needed for adding to the already voluminous literature on the method as proposed by Pemberton[2] and modified by Kilgore, it is found[3] in the action taken by the Association of Official Agricultural Chemists at their last meeting. The method, as modified by Kilgore, gave almost uniformly excellent results on known solutions, in a two years trial in the hands of a number of analysts, and only failed to become

[1] This was so low as to necessitate filtering through asbestos in order to see end reaction by Volhard's method.

[2] This Journal, 15, 382.

[3] Bul. 43, Div. Chem. U. S. Dept. Agr., 104.

an official method because many of the members had not worked with it.

During the past fall the writer has used the Kilgore modification as a check in quite a number of gravimetric determinations with very satisfactory results. While this modification may be considered as accurate as the molybdate for this class of work, at least on low percentages and in careful hands, it was felt that if the exact time and temperature elements could be gotten rid of, there would be a saving of both time and care where a large number of determinations were to be made. With this end in view, it was determined to study the following points:

1. The method of filtering and washing.
2. The time of standing after adding the molybdate solution.
3. The use of tartaric acid to prevent the precipitation of molybdic acid.

With regard to the first point it was found desirable to use simply the paper and funnel, doing away with the use of pressure and filtering twenty at a time. To simplify washing the dilute nitric acid and three per cent. potassium nitrate were omitted from the washings.

As the filter paper and funnel have been used with pressure with satisfactory results, there seems to be no objection to the use without pressure, so to condense the work as much as possible, the subjects were studied in pairs, as follows:

A. The method of filtering and washing and the time of standing after adding the molybdate solution.

B. The method of filtering and washing, and the use of tartaric acid to prevent the precipitation of molybdic acid.

A. THE EFFECTS OF THE METHOD OF FILTERING AND WASHING AND THE TIME OF STANDING AFTER ADDING THE MOLYBDIC SOLUTION.

After some preliminary work, during which the volumetric method, as carried out at the New Jersey Station,[1] was tried and found to work very satisfactorily, it was determined to try the effect of standing for one half hour and for one hour at from 40°–50° C. It was thought best to allow some range of tempera-

[1] Bul. 43, Div. Chem. U. S. Dept. Agr., 92.

ture, as the care required to maintain a constant temperature is considerable.

The molybdate used was the official solution, to which ten cc. 1.42 sp. gr. nitric acid per cubic centimeter had been added. After standing the required length of time, the solutions were filtered off without pressure, the precipitates washed three times by decantation, allowing the precipitate to settle each time before decanting, the precipitates then transferred to the filters, the beakers washed out thoroughly and the precipitates washed until the wash water was neutral to litmus paper, which required from 200 cc. to 300 cc.; this latter amount has been found to free the precipitate from adhering acid in every instance. To feel sure that no appreciable amount of acid was retained in the filter, the washing was continued in a number of cases after no reaction was given with litmus paper, the washing received in clean beakers and titrated with the standard solutions. Table I gives the amount of acid removed by this extra washing as expressed in percentages of P_2O_5.

TABLE I.—THE AMOUNT OF ACIDITY EXPRESSED AS P_2O_5 RETAINED IN PRECIPITATES AFTER WASHINGS WERE NEUTRAL TO LITMUS PAPER.

Number.	Amount of washing until neutral to litmus paper.	Amount of washing after neutral to litmus paper.	Amount of acidity in last wash water, expressed as P_2O_5.	Per cent. P_2O_5 in precipitate on filter.	Remarks.
	cc.	cc.	Per cent.	Per cent.	
1	140	50	0.00	2.14	
2	135	"	0.01	2.81	
3	140	"	0.01	1.88	
4	200	"	0.04	1.48	Blue on fil-
5	150	"	0.00	2.52	ter hard to
6	225	75	0.05	9.68	free from
7	"	"	0.025	12.93	acid.
8	"	"	0.025	6.46	
9	"	"	0.025	15.35	
10	"	"	0.000	15.28	
11	"	"	0.000	10.10	
12	"	"	0.000	17.09	
13	"	"	0.000	17.65	
14	"	"	0.025	22.10	
15	"	"	0.015	20.77	

Average.............. 0.016 per cent.

These results show that when the washings become neutral to litmus paper, the precipitates are practically free from acid. It may be well to call attention to the fact that a first-class grade of filter paper should be used, otherwise the precipitate may run through the filter.

In Table II the results obtained when the solutions stood one-half and one hour and were then treated as above mentioned are compared with the gravimetric.

TABLE II.—COMPARISON OF TIME OF STANDING.

Stood one-half hour at 40°-50°.					Stood one hour at 40°-50°.				
Number.	Washings.	Per cent. standing one-half hour.	Per cent. gravimetric.	Difference + or − from gravimetric.	Number.	Washings.	Per cent. stood one hour.	Per cent. gravimetric.	Difference + or − from gravimetric.
1	200	0.50	0.58	−0.07	1	200	1.84	1.75	+0.09
2	"	2.58	2.42	+0.16	2	"	1.96	1.79	+0.17
3	"	2.86	2.74	+0.12	3	"	2.38	2.38	0.00
4	"	2.06	2.17	−0.11	4	"	2.14	2.03	+0.11
5	"	2.10	2.17	−0.07	5	"	1.58	1.47	+0.10
6	"	5.00	5.06	−0.06	6	"	2.56	2.74	−0.18
7	"	4.41	4.56	−0.15	7	"	4.87	4.78	+0.09
8	"	3.06	3.08	−0.02	8	"	1.39	1.39	0.00
9	"	1.89	1.88	+0.01	9	"	2.08	2.07	+0.01
10	"	0.59	0.61	−0.02	10	"	2.88	3.06	−0.18
11	"	3.42	3.32	+0.10	11	"	2.40	2.54	−0.14
77	"	1.69	1.56	+0.12	12	"	3.43	3.25	+0.18
					13	"	3.18	3.33	−0.15
					14	"	1.42	1.39	+0.03
					15	"	1.01	0.91	+0.10

Stood one-half hour: Average difference..... 0.085
Difference of averages. + 0.0016

Stood one hour: Average difference..... 0.102
Difference of averages..+0.015

From these results it appears that standing as long as one hour before filtering does not give results differing from the gravimetric more than the allowance for duplicates by that method. These results are not what was to have been expected from Kilgore's[1] experiments with various molybdates, as he found that both the official solution and that used by Pemberton gave deposits of

[1] Bul. 43, Div. Chem., U. S. Dept. Agr., 103.

molybdic acid in less than half an hour when heated to 60°. This difference is possibly explained by the fact that the ratio of nitric acid to the molybdic acid in solution was much greater than in his experiments, due to the precipitation of most of the molybdic acid by the phosphoric acid present.

B. THE EFFECT OF THE METHOD OF FILTERING AND WASHING AND THE USE OF TARTARIC ACID TO PREVENT THE PRECIPITATION OF MOLYBDIC ACID.

Jüpner's[1] experiments indicate that the precipitation of molybdic acid may be entirely prevented by the use of tartaric acid; also that the higher the temperature of precipitation the more tartaric acid required to keep the molybdic acid in solution.

Kilgore,[2] whose results are published since this work was done, comes to the conclusion that the use of citric acid for this same purpose possesses no advantage over the official molybdate solution, to which ten cc. of nitric acid per hundred has been added, and requires much longer time for the complete precipitation of the ammonium phosphomolybdate.

In the work given below the official molybdate solution plus ten cc. nitric acid and one gram tartaric acid per 100 cc. was used. A very little work soon proved that adding the molybdate to the phosphate solution at 30°, and allowing to stand one hour at the temperature of the laboratory, will not give satisfactory results, and standing one hour at 30°, gave very little better results, the ammonium phosphomolybdate remaining in solution and precipitating some time after running through the filter. Standing over night in the cold, however, gave excellent results, on low percentages, upon which alone it was tried. It was next determined to try the plan of allowing solutions to stand at 40°–50° for one hour and for two hours; the results, which are in most instances, comparable with those obtained by the gravimetric method, are given, with the results by the method of allowing to stand over night, in Table III.

[1] Abs. Expt. Record, 6, 610.

[2] This Journal, 17, 960.

TABLE III.—COMPARISON OF TIME OF STANDING, USING MOLYBDIC SOLUTION CONTAINING TARTARIC ACID.

Stood one hour at 40°-50°.					Stood two hours at 40°-50°.					Stood over night in the cold.				
Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or − from volumetric.	Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or − from volumetric.	Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or − from volumetric.
1	250	4.76	6.35 6.20	−1.51	1	275	1.40	1.33	+0.07	1	200	0.99	0.92	+0.07
2	"	2.54	2.38	+0.16	2	"	0.94	1.20	−0.26	2	"	2.14	2.16	−0.02
3	"	1.48	1.64	−0.16	3	"	0.65	0.50	+0.15	3	"	0.76	0.79	−0.03
4	"	2.41	2.57	−0.16	4	"	3.15	3.26	−0.11	4	"	1.35	1.32	+0.03
5	"	4.79	6.75 6.82	−2.00	5	"	2.77	2.85	+0.19	5	"	0.42	0.44	−0.02
6	"	1.81	2.28	−0.47	6	"	1.58	1.50	+0.08	6	"	1.70	1.65	+0.05
7	"	1.91	1.96	−0.05	7	"	2.20	2.08	+0.12	7	"	2.81	2.88	−0.07
8	"	2.22	2.06	+0.06	8	"	2.49	2.42	+0.07	8	"	1.12	1.12	0.00
9	"	0.72	0.69	+0.03	9	"	2.48	2.32	+0.16	9	"	1.56	1.49	+0.07
10	"	0.90	1.35 1.32	−0.44	10	"	2.28	2.40	−0.12	10	"	1.68	1.65	+0.03
					11	"	2.18	2.39	−0.19	11	"	1.18	1.10	+0.08
										12	200	2.52	2.55	+0.07

From these results it would appear that standing at 40°–50° for one hour is not to be relied on, at least for low percentages, the results in all cases being too low. Standing at 40°–50° for two hours, however, tends to give results slightly higher than those obtained by the volumetric method, while standing in the cold over night gives results practically identical with it.

This work of determining the temperature and time of standing that would probably give the best results, was done with low percentage solutions, as they were the most convenient at the time.

The figures so far obtained indicated that for further study with the official molybdate solution containing ten cc. of nitric acid extra, standing one-half hour at 40°–50°, was to be preferred, as standing for one hour tends to slightly high results.

It is believed, however, that standing for one hour will still give results comparable with results by the gravimetric method, but the precipitates require more washing, and longer time is required to complete the determinations.

For the further study of the use of tartaric acid, standing at 40°–50° for two hours, was selected.

For this final comparison of the various modifications solutions of fertilizers in which the phosphoric acid had been carefully determined gravimetrically by Mr. W. W. Skinner, were used. The samples cover practically all grades of commercial fertilizers, and have quite a range in percentage of phosphoric acid. The solutions and precipitates in both modifications were treated alike in all cases, except the time of standing.

TABLE IV.—COMPARISON OF VARIOUS MODIFICATIONS WITH THE GRAVIMETRIC.

Number.	One gram tartaric acid per 100 cc. molybdate two hours at 40°–50°.	Official molybdate + ten cc. HNO_3 per 100 cc. one-half hour at 40°–50°.	Gravimetric. (Skinner).	Volumetric.	Difference + or − from gravimetric. Titrated. Molybdate.	Difference + or − from gravimetric. Official molybdate + ten cc. HNO_3 per 100 cc.
1	9.73	9.68	9.75	....	—0.02	—0.07
2	15.65 15.42 (12.85)[1]	15.35	15.34	15.45	+0.16	—0.01
3	13.05 13.15	12.93	13.06	....	+0.04	—0.13
4	6.60 6.68 [2]	6.48[2] 6.43[3]	6.30	....	+0.34	+0.16
5	13.35	13.23	13.35	....	0.00	0.07
6	10.00 9.95 (10.33)[1]	10.10 10.20	10.19	....	—0.21	—0.00
7	17.10 17.20	17.03 17.15	17.40	16.93	—0.25	—0.31
8	17.70 17.68	17.60 17.70	17.94	17.65	—0.25	—0.29
9	22.08 22.08	22.10	22.29	22.15	—0.21	—0.19
10	20.95	22.68 20.85	20.85	....	+0.10	—0.07
Average	14.617	14.541	14.647		0.156	0.141
		Difference of averages	....		—0.03	—0.10

In several instances where the modified methods gave decidedly lower results than the gravimetric method, the determinations were also made by the Kilgore modification, the results

[1] Omitted from averages.
[2] Fifteen cc. molybdate used.
[3] Ten cc. molybdate used.

agreeing in all cases with the results by the modified methods.

The results agree fairly well with the reported results by the Kilgore method, which averages slightly lower than the gravimetric results. The average difference by these modifications is 0.156 and 0.141 per cent., and the average of the plus and minus differences is 0.03 and 0.106 by the titrated molybdate and by the Kilgore molybdate respectively.

Only two results are noticeably higher than the gravimetric, and only one of these differs by more than two-tenths per cent. This seems to be due to the presence of a great excess of molybdate, as it will be noticed that when less molybdate was used the result was nearer the gravimetric. From the observation of quite a number of results, the writer believes that the amount of molybdate added should not be more than enough to precipitate one and a half times the phosphoric acid found to be present, otherwise the results are too high.

From the figures presented the following conclusions may be drawn:

1. The molybdate solution, to which nitric acid has been added, standing one-half hour at 40°–50°, gives results comparing very favorably with the gravimetric.

2. While the use of tartaric acid in the molybdate solution gives good results, it possesses no advantage and the extra time of standing makes it not so desirable.

The official molybdate plus ten cc. nitric acid per 100 cc., using the funnel and paper without pressure in filtering, and only water for washing is preferred by the writer to the usual way of carrying out the volumetric method; this admits of a better distribution of the work, which makes in his hands a more rapid method where a large number of determinations are to be made.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 18.]

INDEX TO THE LITERATURE ON THE DETECTION AND ESTIMATION OF FUSEL OIL IN SPIRITS.

BY W. D. BIGELOW.

Received September 20, 1895.

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THE OCCURRENCE OF TITANIUM.

BY CHARLES E. WAIT.

Received February 11, 1896.

IT is not my present purpose to repeat what has been already frequently published relative to the presence of titanium in minerals, typical rocks, meteorites, clays, soils blast furnace products, etc. I wish merely to call attention to the fact that some of the bodies with which we have much to do contain titanium, and that probably owing to the difficulties formerly

experienced in its estimation, it has been more frequently overlooked than is generally supposed.

In the recent examination of food materials, under the direction of the United States Department of Agriculture, I have had occasion to make analyses of the ashes of some plant materials, and this having led to further investigations, I was interested and surprised to find titanium present in every plant ash thus far examined.

This is in fact surprising, as it is stated by some writers[1] that "it does not appear to form part of the animal or vegetable kingdom."

The amount of titanic oxide found in the ash of some vegetable material is as follows:

	Per cent.
Oak wood	0.31
Apple and pear wood mixed	0.21
Apple	0.11
Cow peas	0.01
Cottonseed meal	0.02

From the above determinations we are reasonably safe in assuming that titanium is assimilated by plants. If this is true, it seems very strange that reference to this fact has not been made by recent writers upon agricultural chemical analysis, and upon the chemistry of vegetable life.

In fact, in consulting treatises on ash analysis with tables,[2] I do not find any mention whatever of the presence of titanium. If this is a fact, can it be true that it has escaped the attention of chemists for so long a time?

The examination of the ash of bituminous and anthracite coal shows the presence of titanic oxide. The results of some determinations are as follows:

	Per cent.
Jellico (Tenn.) bituminous coal	0.69
Coal Creek (Tenn.) bituminous coal	0.95
Pocahontas (Va.) bituminous coal	0.94
Middlesborough (Ky.) bituminous coal	0.83
Pennsylvania anthracite coal	2.58

1 Roscoe & Schlorlemmer.
2 Wolff.

With reference to the presence of titanic oxide in the ash of coal, it may be fairly assumed that partly owing to the infiltration of clay and earthy materials, it would be found there, but is it fair to assume that its presence is wholly accounted for in that way? If mention has been made of the presence of titanium in the ash of coal, it has thus far escaped my attention.

The method employed in the above determination is that of A. Weller,[1] which is based upon the fact that hydrogen peroxide, when added to a solution of titanium, produces a compound of an intensely yellow color. There are precautions necessary in the execution of this method which have already been pointed out.[2]

It will be my pleasure to report additional notes at an early day concerning the presence of titanium in the vegetable kingdom. Valuable service has been rendered in the above work by Messrs. J. O. LaBach and C. O. Hill.

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THE ESTIMATION OF PYRRHOTITE IN PYRITES ORES.

BY EDWIN F. CONE.

Received January 22, 1896.

SOME of the American pyrites ores contain the mineral pyrrhotite (Fe_7S_8) in varying proportions. In the manufacture of sulphuric acid from these ores it is found impossible to burn out at least the greater part, if not all, of the sulphur which is present as pyrrhotite. In the estimation of total sulphur in the sample of such an ore, of course the sulphur present as pyrrhotite is included. It is therefore necessary, in order to make a settlement with the company selling the ore and also in order to figure the yield of acid, to estimate the sulphur present as pyrrhotite as accurately as possible. Authorities give no method to meet the conditions. After a careful investigation of the matter I have perfected the following method; I am indebted to Mr. Lucius Pitkin, of New York City, for some valuable suggestions. It is based on the fact that Fe_7S_8 is magnetic, pyrites being non-magnetic.

[1] *Ber. d. chem. Ges.*, 1882.

[2] This Journal, 13, 210.

Method.—After the ground sample has been passed through a sixty mesh seive, 13.74 grams are weighed and spread out upon a good-sized sheet of glazed paper. A magnet is passed through and over this several times, the magnetic portion being carefully separated from the magnet by first stroking suddenly the top of the magnet, which dislodges most of the mechanically admixed pyrites, and then, secondly, separating the magnetic portion by means of the armature and a brush. The process is carried out five or six times, enough separations having been made to have reasonably separated all the magnetic portion. This is then finely ground in an agate mortar and the sulphur estimated gravimetrically by oxidation with nitric and bromohydrochloric acids. The weight of barium sulphate obtained in grams is the percentage of sulphur present as pyrrhotite.

The accuracy of this method was proved by the following work:

A sample of ore containing a known percentage of pyrrhotite was obtained. It analyzed as follows:

	Per cent.
Total sulphur	35.07
" Iron	57.50
Oxygen as Fe_3O_4	4.26
Copper	0.25
Insoluble matter	2.78
	99.86

Sulphur present as Fe_7S_8	24.14
Iron " " Fe_7S_8	36.96
" " " FeS_2	9.34
Sulphur " " FeS_2	10.68
Iron " " Fe_3O_4	11.20

A sample of pyrites containing no pyrrhotite nor magnetic portion was then obtained. To a definite portion of this I added enough of the ore containing pyrrhotite to give 1.20 per cent. of sulphur present as pyrrhotite in the mixture; *i. e.*, to fifty grams of the pyrites I added 2.63 grams of pyrrhotite ore, or

$$\frac{24.14 \times 2.63}{52.63} = 1.20 \text{ per cent. sulphur as } Fe_7S_8.$$

This mixture was then analyzed for sulphur present as pyr-

rhotite by the method described above, using different weights. Some of the results obtained are :

5.00 grams	gave	0.4120	barium sulphate	= 1.13	per cent.	sulphur	as Fe_7S_8.
13.74 "	"	1.1300	" "	= 1.13	"	"	" Fe_7S_8.
25.00 "	"	2.1570	" "	= 1.18	"	"	" Fe_7S_8.

Others were equally concordant.

The method was also applied to the pyrrhotite, as mentioned above, using portions of one gram or one-half gram giving respectively 24.13 per cent. and 24.15 per cent. sulphur as Fe_7S_8.

This method is accurate to within two-tenths per cent. on ores containing much or little pyrrhotite. The ore must not be finer than that which will pass through a sixty mesh sieve; if it is, results will be unreliable.

Another method, which I used until the perfection of this one, is based upon the fact that Fe_7S_8 gives off hydrogen sulphide with dilute acid, whereas FeS_2 (pyrite) does not. This is reliable when no other sulphides are present, but as most pyrites contain blende the results are usually unreliable.

CLEVELAND, O.

DROWN'S METHOD OF DETERMINING SULPHUR IN PIG IRON.

BY GEORGE AUCHY.
Received February 26, 1896.

Of the various evolution methods of determining sulphur in pig iron, Drown's is perhaps the best. Methods in which the sulphur is precipitated in any other form but barium sulphate (cadmium sulphide for instance), are not so convenient for the reason that the sulphur in the graphitic residue must be determined as barium sulphate. A slight drawback, however, attaches to the method in that the evolution of the gas must not be allowed to proceed too rapidly, and it is an object of this note to point out that by the use of potassium hydroxide solution in conjunction with the potassium permanganate solution as an absorbent for the gas, this caution is made unnecessary, and the gas may be passed through the solution as rapidly as it is possible to make it do so, without danger of loss; a mixed solution of caustic potash and potassium permanganate possessing stronger oxidizing power, than a solution of the latter salt alone. For there is a tendency in such a mixture, even

when no reducing agent is present, to the liberation of an atom of oxygen and a reduction of the potassium permanganate to potassium manganate, by the union of a molecule of potash with a molecule of potassium permanganate.

$$K_2O.Mn_2O_7 + K_2O = 2K_2MnO_4 + O.$$

If a very large excess of caustic potash solution be added to a few drops of potassium permanganate solution, the reduction to green potassium manganate will be seen to take place immediately. But in a mixture of equal or nearly equal parts of the two solutions, the change is very slow and gradual, except a reducing agent be present.

Convenient proportions of the two solutions for use as an absorbent in the determination of sulphur in pig iron are obtained by using in each case six cc. of a caustic potash solution, made by dissolving six sticks of the solid hydroxide in 350 cc. water, and six cc. of a permanganate solution containing about ten grams of the crystallized salt to the liter of water.

These volumes of the two solutions are carefully withdrawn from the bottles containing them by pipettes, so as to avoid getting any of the sediment at the bottom of the bottle; mixed in a small beaker, and drawn into a Troilius bulb, which is then connected with the evolution flask containing the drillings. The solution of the pig iron may be accomplished in five or ten minutes without any hydrogen sulphide passing through the caustic potash and permanganate solution unabsorbed. The purple color of the permanganate gradually changes to the green of the manganate, which latter solution is also a stronger oxidizing agent than permanganate.

Not an inconsiderable convenience also in the use of this mixed solution is in the fact that the oxide of manganese separating out does not adhere to the glass tenaciously, and may be washed out with water instead of requiring to be dissolved out by strong hydrochloric acid and added to the main solution.

The next step in Drown's method is getting the manganese in colorless solution preparatory to the precipitation by barium chloride. This is accomplished by evaporation to dryness with hydrochloric acid, and separation of silica; or by adding enough hydrochloric acid to get the clear solution by the aid of heat, but

without the tedious evaporation to dryness, and afterwards neutralizing the excess of acid with ammonia. The writer would suggest the use of oxalic acid in connection with hydrochloric acid, as by its use the solution of the manganese oxides is effected almost instantaneously and without the use of an excess of hydrochloric acid, a very small amount of the latter sufficing, and the barium chloride precipitation may then at once take place.

In detail: Take 3.4335 grams of the pig-iron drillings in a sixteen-ounce gas flask and connect with the Troilius bulb containing the mixed solution of caustic potash and potassium permanganate, as described. Pour through the funnel tube dilute hydrochloric acid in not unnecessary amount, and bring quickly to a boil. Then push to a cooler part of the plate and aspirate air through. A convenient arrangement is to have a narrow upright board fastened to the desk, or on a stand next to the filter pump; on the other side of the board stands the iron plate. This upright board, standing edgewise to the plate, is provided with nails or hooks for the support of the Troilius bulbs which are hung one above the other. Three or four determinations can be carried on at once in this way with the greatest possible economy of desk room. The aspirating is done by the filter pump.

Transfer the contents of the Troilius bulb to a small beaker, washing out with water. Filter the solution in the evolution flask through a ribbed filter and wash with hot water. Then punch a hole in the paper and wash the graphite and silica into an evaporating dish. Evaporate to dryness. Add thirty cc. aqua regia. Evaporate to dryness. When dry, add eight to ten cc. dilute hydrochloric acid. Heat, dilute with hot water and filter into the solution washed out of the Troilius bulb. Bring this solution then to a boil, add enough oxalic acid to clear the solution, (a very little will suffice), then five cc. barium chloride solution and boil about an hour. Allow to stand over night. The barium sulphate found, multiplied by four, will give the percentage of sulphur in the pig.

Caustic potash solution always contains considerable amounts of dissolved silica (for instance, in six cc. the amount used in a determination was found to be 0.0051 gram). But it is not

necessary to separate it, as a recent writer in the *Chemical News* has shown that precipitated barium sulphate is not contaminated by silica in solution, and the following experiments also show it. In these experiments a standard solution of sulphuric acid was used; mixed in each case with the amounts of caustic potash solution, and permanganate solution that are used in a regular determination. Instead of using ten cc. of hydrochloric acid, however, twenty cc. were used, but afterwards made alkaline with ammonia, then hydrochloric acid added drop by drop till just acid again, and the solution filtered from the alumina remaining undissolved. Then precipitated by barium chloride. Also the excess of oxalic acid used to bring the manganese oxides into solution was destroyed by permanganate solution before the neutralization and precipitation and the slight excess of permanganate by a piece of fine iron wire and stirring. The barium sulphate found was, for convenience in each case, calculated as though the usual amount of drillings had been taken, and a regular determination had been made.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.237	0.238
" 2	0.121	0.119
" 3	0.057	0.057
" 4	0.029	0.033

To note the effect of precipitating in a strongly acid solution, and one which therefore required no filtration from alumina before precipitating, the following tests were made as before, but with ammonia added to leave five cc. of free hydrochloric acid at time of precipitation (excess of oxalic acid again destroyed).

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.121	0.112
" 2	0.121	0.114
" 3	0.237	0.234
" 4	0.057	0.054
" 5	0.029	0.029
" 6	0.014	0.010
" 7	0.029	0.028
" 8	0.029	0.026
" 9	0.014	0.010

These results show a very marked tendency to lowness. The following were then made, using ten cc. of hydrochloric acid for solution of the manganese oxides (together with oxalic acid, the excess of the latter, however, afterward destroyed by adding permanganate solution), and without any after neutralization with ammonia whatever, the solution therefore containing *over* five cc. of free acid, but no ammonium chloride.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.014	0.014
" 2	0.029	0.029
" 3	0.121	0.115

At this point it was thought well to also try the effect of oxalic acid upon the precipitation. It was feared it might have a solvent action upon the barium sulphate, especially in strongly acid solutions. In other respects the conditions were the same as in the series immediately preceding—ten cc. hydrochloric acid, no ammonia, etc., but excess of oxalic acid *not* destroyed.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.014	0.014
" 2	0.029	0.029
" 3	0.121	0.118
" 4	0.029	0.029
" 5	0.060	0.059
" 6	0.090	0.090
" 7	0.045	0.046
" 8	0.060	0.060
" 9	0.090	0.090
" 10	0.029	0.029
" 11	0.014	0.014
" 12	0.121	0.119
" 13	0.237	0.239

From these results it would seem that the oxalic acid helped rather than hindered the precipitation of barium sulphate.

To see if there was any tendency of barium oxalate to precipitate, a test was made under conditions identical with No. 13, except that the solution was neutralized with ammonia till merely faintly acid before precipitating. Result 0.239 per cent., or just the same as in the strongly acid test. Showing no tendency of barium oxalate to precipitate.

Again, in standard solution equivalent to 0.121 per cent. taken, ten cc. hydrochloric acid added, brought to a boil, and precipitated with barium chloride. Result 0.119 per cent. Then the test repeated twice with addition of oxalic acid. Results, No. 1, 0.120 per cent., No. 2, 0.120 per cent.

Thinking perhaps good results could also be obtained by allowing the precipitated barium sulphate to stand only one hour before filtration, the following tests were made (ten cc. hydrochloric acid, no ammonia, excess of oxalic acid not destroyed).

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.029	0.024
" 2	0.014	0.007
" 3	0.029	0.023
" 4	0.121	0.115
" 5	0.060	0.056
" 6	0.045	0.041

Showing that one hour's standing is not sufficient. But the loss seems so uniform that in cases of hurry it would be perhaps safe to allow only one hour for standing, making afterward a correction in the result of 0.005 per cent.

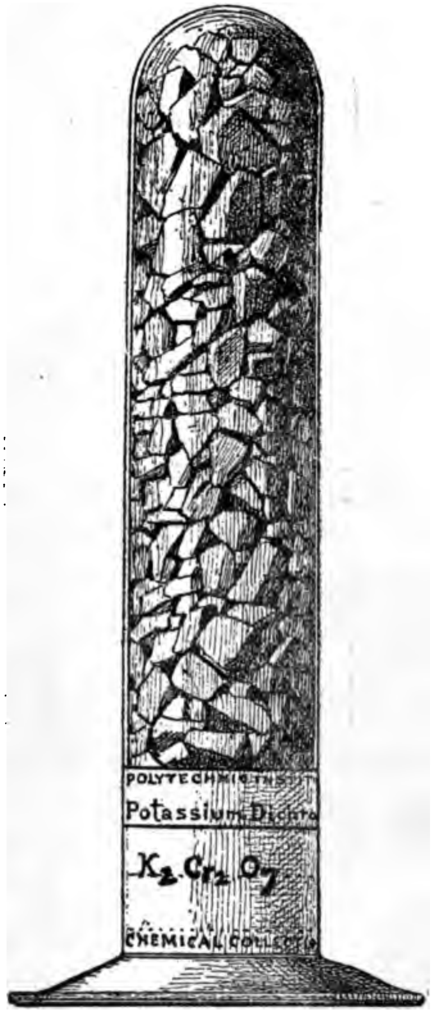
It is important to make a blank or dummy test with the reagents used. In this test use double the reagents and precipitate in nearly neutral solution.

In the regular determinations also precipitations may of course take place in nearly neutral solutions if so desired, and as is usually recommended. The results of the second series, however, may perhaps be taken as a warning against the presence of ammonium chloride in *strongly* acid solutions, and the ammonia should therefore be added to near neutralization if used at all.

In filtering off the barium sulphate it is not advisable to use a rapid filtering funnel, as barium sulphate equal to 0.002 or 0.003 per cent. is more than likely to pass through the filter paper and escape notice in the filtrate, except the liquid be stirred in such a way as to collect it together in the middle of the bottom of the beaker. When hydrochloric acid is spoken of in this article the dilute acid (equal parts water and acid) is meant.

NOTE.

A New Specimen Bottle.[1]—There are several reasons why glass-stoppered bottles are well adapted for small specimens. The neck and stopper form an awkward cover looking to the specimen. The neck is usually too small in proportion to the width of the bottle, and as a specimen is not intended to be taken out of its receptacle, the stopper and ground neck are inappropriate. But the chief objection to their use is their cost.



FULL SIZE.

The form which I have found to be very practical consists of a tube with a rounded top provided with a flanged base. This form is pleasing to the eye, exhibits the whole of the specimen, is not easily upset, is air- and moisture-tight, and is low priced.

In filling the tube, it is inverted, and when enough of the specimen has been put in, a cylindrical (not conical cork) is pushed in. When the specimen does not pack, or when but few crystals are placed in the tube, it is well to paste a disk of white paper in the top of the cork, so as to conceal it from sight. In the case of colorless crystals, glazed black paper gives a better effect. The

[1] Read before the New York Section, October 4, 1895.

cork should be driven in so as to leave about one-sixteenth of an inch space below the jointure of the tube and the flange. Melted paraffin is then poured in. A layer a quarter of an inch thick is quite enough to exclude air and moisture and to hermetically seal the tube. If desirable, the whole space of the base may be filled with paraffin, and, when cool, the wax may be pared down flat with a knife long enough to touch both sides. The addition of a little lampblack to the paraffin makes a better effect. The label is then put on. It should be long enough to give a slight lap and wide enough to cover the cork. The top of the cork should be just level with the edge of the label. The inside of the base flange may be painted with black varnish, or it may be made of black or colored glass.

The flanged base prevents the tubes from touching each other, and thus shows off the samples very effectively. It is well to arrange the shelves in stairs. The steps may be three inches wide and two and a half inches high. The rows should be alternate, so that the labels of each row but the first may be seen between the tubes of the row in front of it.

When a small amount or a single crystal of a specimen is to be exhibited, a good effect can be produced by thrusting a copper wire into the cork and twisting the other end into a circle about half an inch in diameter. On this is placed a three-fourths of an inch watch glass, and in this the specimen. The stalk of the support should be about two inches long. Other modifications will naturally occur to any one.

As the operations involved in making these specimens are few and simple, their cost is low in comparison with the ground glass-stoppered bottles. Whitall and Tatum make the size represented in the cut for $7.00 a gross in four gross lots, which is a shade less than five cents a piece. Larger or smaller sizes can be furnished at proportional prices.

PETER T. AUSTEN.

BROOKLYN POLYTECHNIC INSTITUTE,
January 15, 1896.

BOOKS RECEIVED.

The Smithsonian Institution: Its Origin, Growth, and Activities. By Prof. Henry Carrington Bolton, Ph.D. New York: D. Appleton & Co. 30 pp.

Handbook of the Bio-Chemical Laboratory. By John A. Mandel. New York: John Wiley & Sons. v, 101 pp. Price $1.50.

Bulletin No. 28. An Important Elm Insect. Reno, Nev.: Agricultural Experiment Station of the Nevada State University. November, 1895. 8 pp.

Bulletin No. 29. The San Jose Scale. Reno, Nev.: Agricultural Experiment Station of the Nevada State University. December, 1895. 8 pp.

Bulletin No. 121. Hillside Terraces or Ditches. Raleigh, N. C.: North Carolina Agricultural Experiment Station. October, 1895. 8 pp.

Bulletin No. 125. Forage Grasses and Hay-Making. I. Tests of Forage Grasses. II. The Formation and Care of Grass Lands. III. Haying Tools and Hay-Making. Raleigh, N. C.: North Carolina Agricultural Experiment Station. January 15, 1895. 41 pp.

Ueber Reindarstellung der Gährungsmilchsäure mit einleitenden Versuchen über Destillation in Vakuum der Quecksilberluftpumpe. Dissertation by Wilhelm A. Dyes, Ph.D. 1895. 44 pp.

ERRATA.

On page 223 (March number) under solution number 3, instead of

Water .... 115 cc.

read

Water .... 190 cc.

and instead of

Phosphoric acid 1.40 sp. gr.............. 315 cc.

read

Phosphoric acid 1.40 sp. gr.............. 340 cc.

VOL. XVIII. [MAY, 1896.] No. 5.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

HYDROFLUORIC ACID.[1]

BY KARL F. STAHL.

Received March 10, 1896.

HYDROFLUORIC acid is always made by decomposing ground fluorspar with sulphuric acid in cast iron vessels and absorbing the resulting fumes of hydrofluoric acid in leaden vessels of varying construction, containing more or less water, according to the strength desired.

The commercial acid, containing forty to fifty-two per cent. hydrofluoric, is stored and shipped in lead vessels, or small quantities in gutta percha bottles. Weaker acid, of about thirty-five per cent. and less, can be stored for a limited time in wood and is sometimes shipped in barrels, usually oil barrels. In this country the so-called "chemically pure" acid is packed in ceresine bottles, which answer very well, but must be kept away from the Bunsen burner, as the melting point of the ceresine is low. In Europe the C. P. acid is shipped either in gutta percha or platinum bottles, but the acid takes up, in course of time, mineral and organic matter from the gutta percha and ceases to be C. P. Platinum bottles are the best, but require a heavy investment.

The impurities, which can hardly be avoided in manufacturing commercial hydrofluoric acid, and are therefore always present, are:

1. *Hydrofluosilicic Acid.*—This is the most important impurity,

[1] Abstracted from a lecture before the chemical section of the Engineers Society of Western Pennsylvania, at Pittsburgh, February 28th, 1896. Communicated by the author.

not because it does any direct harm in the application of the acid, but because the fluorine combined with silica is perfectly useless. The source of the hydrofluosilicic acid is free or combined silica in the fluorspar, which is all dissolved and volatilized by the hydrofluoric acid. It seems almost impossible to obtain spar free from silica. American ground fluorspar contains usually about one and a half per cent.; samples of English spar, which I have tested, were even higher in silica, about three per cent., while six samples of German spar contained from one-tenth to seven-tenths per cent. silica. In the rapid determination of silica in fluorspar an analytical problem presents itself, which I have not yet solved to my satisfaction. I use the following extremely simple method:

One gram of ground fluorspar, in a platinum dish, with a small platinum spatula, is dried at about 130° C., weighed exactly, moistened with hydrofluoric acid, stirred with a spatula, evaporated to dryness on the water-bath; this is repeated, then dried again at 130° C., and weighed. The difference I assume to be silica, which is only correct when free silica is present, but the spar may contain silicates, for instance clay; in that case a fluoride of aluminum would be formed, part of the weight of the silica would be replaced by the weight of the fluorine retained and the silica be found too low. If carbonates are present the error would not be great, for instance,

$$CaCO_3\ (100) \text{ would give } CaF_2\ (78),$$

and the silica be found too high. The presence of carbonate is, however, easily detected, and the carbonate can be removed with acetic acid. Galena is often present in small quantities and gives the spar a grayish or bluish color, in that case

$$PbS\ (239) \text{ would give } PbF_2\ (245),$$

an error that would not be perceptible. This simple method, to which any careful boy can be drilled in a short time, is therefore likely to give quite accurate results.

The great damage done by silica in the spar is plainly shown by the following equation:

$$(1)\quad \underset{60}{SiO_2} + \underset{234}{3CaF_2} + \underset{294}{3H_2SO_4} = \underset{144}{SiF_4(HF)_2} + \underset{408}{3CaSO_4} + \underset{36}{2H_2O}.$$

For every part of silica about four parts of fluorspar and five parts of sulphuric acid are wasted, or expressing it in money value, for every per cent. of silica at least ten per cent. (four per cent. for spar and about seven per cent. for sulphuric acid) should be deducted from the value of the spar.

2. *Sulphuric Acid*, which is distilled over in small quantities out of the decomposing vessel, does no harm in the application of the hydrofluoric acid for etching glass or pickling iron. But in analyzing the acid it must be determined, otherwise it would be figured as hydrofluoric acid.

On evaporation and calcining, commercial acid should leave but a trace of non-volatile matter.

About five years ago, having made some hydrofluoric acid in an experimental apparatus, I was confronted with the inability to tell what I had made; that is, I could not find a method which would have enabled me to determine the composition in a reasonably short time.

The methed of determining quickly the percentage of a liquid by its specific gravity is of little value for two reasons, first, because the methods for determining the specific gravity of other liquids can only be used with modifications for hydrofluoric acid, as they involve the use of a glass instrument of some kind. A glass hydrometer can only be used a few times until the acid has ruined it; picnometers are out of the question; even the temperature of hydrofluoric acid cannot be determined directly with a thermometer, as soon as a glass thermometer is placed into the acid the mercury begins to rise from the heat evolved by the action of the acid on the glass. I use, therefore, a platinum hydrometer. A hydrometer made from pure silver would probably last a long time. I have seen one made out of German silver plated with silver, but the hydrofluoric acid got through the plating and ate numerous pinholes into the instrument.

The impurities mentioned above, *i. e.*, hydrofluosilicic acid and sulphuric acid, influence the specific gravity of the hydrofluoric acid to a marked degree, so much that the determination of the specific gravity of an acid of unknown origin is of little value, but for controlling the process in the works, where the

character of the raw materials and the degree of purity of the produced hydrofluoric acid is known, it is of value, provided the conclusions drawn from it are from time to time verified by an analysis. It will not do to depend too much on the specific gravity.

Without taking up any time with a description of the experiments, which led finally to the method I use, I will give the latter in detail.

The samples are brought to the laboratory in lead cylinders of convenient size, with a handle. These are placed in water of 15° C., often remaining there for at least five minutes; the specific gravity is taken; then with the aid of a small platinum tube, serving as a pipette, and chips of filtering paper, to remove a small excess, three portions are weighed out:

1. Two grams in a very small platinum crucible (holding about five cc).

2. Two grams in a large platinum crucible (holding about forty cc.)

3. Four grams in a small platinum dish.

A. TOTAL ACIDITY.

Place the small platinum crucible, covered with its lid, in a large platinum dish (holding about 100 cc.), then run, according to the expected percentage, twenty-five or fifty cc. normal caustic solution (forty grams caustic soda per liter) from a pipette into the dish, upset the covered crucible, and mix the acid and alkali with a platinum stirrer; add two drops of a solution of phenolphthalein (1 gram in 100 cc. alcohol) and then add more of the normal soda solution from a burette till the colorless liquid assumes the characteristic bright red color. Place over a Bunsen burner and heat to about 50° C; the red color will disappear. Finally add normal solution from the burette slowly till the red color remains constant when heated, which indicates that all free sulphuric acid, hydrofluoric acid, and hydrofluosilicic acid have been neutralized. The number of cubic centimeters used we call "*a*."

If litmus is used in place of phenolphthalein, the soda solution has to be added till the color is perfectly blue, but the end of the

reaction is indistinct, while with phenolphthalein as indicator it is very sharp.

B. HYDROFLUOSILICIC ACID.

To the acid in the large platinum crucible (two grams) add five cc. water (measured approximately), then slowly about two grams[1] potassium carbonate either in small pieces or in concentrated solution, add about fifteen cc. of fifty per cent. alcohol and then as many cubic centimeters of ninety-five per cent alcohol as water used, which will bring the whole to a volume of about twenty-five cc. containing about fifty per cent. alcohol,[2] let it stand for at least one hour. Filter[3] and wash the gelatinous precipitate, consisting of potassium silicofluoride, with fifty per cent. alcohol till blue litmus paper ceases to be turned red by the filtrate. Throw the filter with the precipitate into a platinum dish, add about twenty-five cc. of water and warm to about 50° C., titrate slowly with normal caustic soda solution and phenolphthalein, as described in the determination of total acidity. The number of cubic centimeters used we call "*b*."

C. SULPHURIC ACID.

Place the platinum dish containing four grams of the acid to be tested, on a water-bath under a hood with a good draft and evaporate till acid fnmes have completely ceased to be given off. Titrate the remaining syrupy liquid, which contains the free sulphuric acid, cold, with normal acid solution, using either litmus or phenolphthalein as indicator. The number of cubic centimeters used we call "*c*."

The reactions involved are as follows:

$$\underset{20}{HF} + \underset{40}{NaOH} = \underset{42}{NaF} + \underset{18}{H_2O}. \tag{2}$$

[1] The amount of potassium carbonate is calculated to neutralize the acids only partly. To avoid an excess it is advisable to test the liquid with litmus paper, which should show a strong acid reaction. But there should be at least enough potash to form potassium silicofluoride with the fluosilicic acid. In analyzing acid of entirely unknown composition I take for every cubic centimeter normal soda solution used for the determination of total acidity 0.05 gram potassium carbonate. Potassium chloride might be used in place of the carbonate, but in that case free hydrochloric acid is formed, in which the potassium silicofluoride is somewhat soluble.

[2] If the liquid contains more than fifty per cent. alcohol, potassium fluoride is precipitated, if much less alcohol, potassium silicofluoride may remain in solution.

[3] I use a platinum funnel because glass funnels are acted on, but that does not influence the accuracy of the method.

$$(3)\quad \underset{144}{SiF_4(HF)_2} + \underset{240}{6NaOH} = \underset{252}{6NaF} + \underset{60}{SiO_2} + \underset{72}{4H_2O}.$$

$$(4)\quad \underset{220}{SiF_4(KF)_2} + \underset{160}{4NaOH} = \underset{168}{4NaF} + \underset{116}{2KF} + \underset{60}{SiO_2} + \underset{36}{2H_2O}.$$

$$(5)\quad \underset{98}{H_2SO_4} + \underset{80}{2NaOH} = \underset{142}{Na_2SO_4} + \underset{36}{2H_2O}.$$

Now the number of cubic centimeters of normal soda solution used in the first titration and called "a" represents the alkali necessary to neutralize the hydrofluoric acid, hydrofluosilicic acid, and sulphuric acid, and in order to find the number of cubic centimeters used for hydrofluoric acid alone, we have to subtract those used for hydrofluosilicic acid and sulphuric acid, but although we used the same weight (two grams) for the determination of the hydrofluosilicic acid, it would not be correct to subtract the number of cubic centimeters used, because in the potassium silicofluoride two atoms of fluorine are neutralized and we only neutralize with normal solution the remaining four atoms, which are combined with silicon. It would therefore have required $b + \frac{b}{2}$ cc. to neutralize the free acid.

Having employed four grams of substance for the determination of the sulphuric acid, the number of cubic centimeters used for that determination must be divided by 2. The number of cubic centimeters used for hydrofluoric acid alone are therefore equal to $a - (\frac{3}{2}b + \frac{c}{2})$ and as each cubic centimeter normal solution indicates 0.020 gram HF and two grams of substance have been used, the number of cubic centimeters found by the above formula express, without further calculation, the percentage of free hydrofluoric acid. Therefore

$$a - (\tfrac{3}{2}b + \tfrac{c}{2}) = \text{per cent. free hydrofluoric acid.}$$

After the foregoing explanation the calculation of the percentage of hydrofluoric acid is an easy matter. One cc. normal sodium hydroxide indicates 0.055 gram potassium silicofluoride, which was obtained from 0.036 fluosilicic acid; having used two grams of substance, 0.036 has to be divided by 2 and multiplied by 100 to get the percentage, or

$$b \times 1.8 = \text{per cent. hydrofluosilicic acid.}$$

The percentage of free sulphuric acid is obtained by multiplying c, the number of cubic centimeters used, by 0.048, dividing by 4 and multiplying by 100, or

$$c \times 1.2 = \text{per cent. free sulphuric acid.}$$

Other free acids, muriatic or nitric acid, which influence the accuracy of the determination, are not likely to occur in commercial hydrofluoric acid and their presence can easily be detected by well-known analytical methods:

To give an idea of the composition of some of the makes of hydrofluoric acid, I have appended a few of the analyses made in the course of five years:

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Specific gravity......	...	1.299	1.264	1.253	1.244	1.264	1.282	1.247	1.234
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Hydrofluoric acid....	39.6	42.2	44.3	48.1	48.6	51.1	54.2	48.6	33.5
Hydrofluosilicic acid.	2.7	14.9	10.1	4.7	5.0	6.8	8.1	6.3	10.6
Free sulphuric acid..	...	0.8	0.8	4.0	1.9	1.4	1.2	0.8	1.6

1. Oct. 1891. Baker & Adamson, C. P. acid in ceresine bottle, 0.005 per cent. non-volatile residue.

2. Oct. 1891. Manufactured by J. C. Wiarda, sample received.

3. Nov. 1891. " " " " sample taken from package of 100 pounds.

4. Jan. 1892. Manufactured by James Irwin & Co., sample of lot of 3500 pounds.

5. Mar. 1892. Manufactured by James Irwin & Co., sample of lot of 3400 pounds.

6. Jan. 1894. Manufactured by Bender & Aldred, sample taken from package of 100 pounds.

7. Jan. 1895. Manufactured by James Irwin & Co., sample taken from tank holding 3000 pounds.

8. Oct. 1895. Manufactured by James Irwin & Co., sample taken from tank holding 3200 pounds, 0.015 per cent. non-volatile residue.

9. Jan. 1896. So-called "pickling acid" sample received from a foundry.

By comparing analyses Nos. 2 and 7 it can be seen what influence hydrofluosilicic acid has in raising the specific gravity; although No. 2 has a higher specific gravity than No. 7, it contains twelve per cent. less hydrofluoric acid, but six and eight-tenths per cent. more hydrofluosilicic acid. Nos. 3 and 6 have the same specific gravity, but No. 6 contains six and eight-tenths per cent more hydrofluoric acid and three and there-

tenths per cent. less hydrofluosilicic acid. The influence of sulphuric acid on the specific gravity can be seen by comparing Nos. 4 and 5.

A great difficulty in the manufacture of hydrofluoric acid is the very disagreeable and dangerous nature of the gaseous and liquid acid. The effects of the fumes on the respiratory organs are more injurious than those of other acids. Still more marked are the effects of the liquid acid on the skin. One drop of acid, although it does not make itself felt for a few hours, will, even on the horny skin of a workman's hand, cause a very painful inflammation in one-half day. Against the fumes the workmen protect themselves by respirators, or by the simpler way, which they usually prefer, of tying a handkerchief over nose and mouth and by greasing the unprotected parts of the face with lanolin. The latter is as effective as vaseline and easier to wash off. Against liquid acid rubber gloves afford protection. If liquid acid comes in contact with the skin it should be washed off at once with water and aqua ammonia, or another alkali, which will prevent injury.

In conclusion, I wish to say a few words about the different applications of commercial hydrofluoric acid.

The oldest, and up to the present time, most extensive application is for etching glass. For this purpose it can be applied in three different ways. In the gaseous form by suspending the articles to be etched over a mixture of fluorspar and sulphuric acid. This is the oldest way of etching and I believe most burettes, graduated cylinders, etc., for laboratory use are still marked in this way. If applied in gaseous form the acid leaves the surface opaque, while the liquid acid leaves the surface smooth and transparent. For the production of an opaque surface with liquid acid many empirical formulas are published and every glass factory, or rather every etching boss, has his own secret formula. But they all aim to produce a mixture of hydrofluoric acid with a fluoride of ammonium, or potassium, or sodium, with which a number of other substances such as sulphuric, acetic, or muriatic acids, or ammonium or potassium sulphate, etc., are mixed, but it seems quite unnecessarily. Hydrofluoric acid prepared for etching opaque goes under the trade name of

"white acid." Lead glass is very rapidly and uniformly etched and acid of forty-five to forty-eight per cent. is usually employed, while lime glass requires a stronger acid and more time. Lately, acid as strong as fifty-two per cent. HF is employed. "White acid" is much more convenient for application than gaseous acid and acts very rapidly; for instance, a lead glass lamp chimney can be rendered opaque by simply dipping it into the acid for one minute. Lime glass, even with acid specially prepared for it, requires about two minutes immersion. It is important that the temperature of the acid and the glass should be about 15° C. Parts of the glass which are to remain unetched, must be protected. For this purpose a number of substances are in use. Asphaltum varnish is usually employed, when the design is printed on paper and then transferred to the glass; for the so-called needle work a mixture of Burgundy pitch and beeswax is used.

A more recent application of hydrofluoric acid is for cleaning castings from sand. These have so far been cleaned, either by mechanical means, or with sulphuric acid, but the first is expensive and neither way, in many cases, satisfactory. The sulphuric acid loosens the sand by dissolving the iron to which it is attached, while hydrofluoric acid dissolves the sand itself and therefore acts more promptly and does not cause any loss of iron. It also dissolves the magnetic oxide formed on the surface of the iron very readily, much more so than sulphuric acid. This latter point is important for castings, which have to be worked afterwards with edged tools, the magnetic oxide being very hard. For cleaning castings, the acid is diluted to about one or two per cent. HF, the pickling can therefore be carried on in wooden vessels.

Some of the firms, who use hydrofluoric acid for cleaning iron, have kindly sent me reports on it. The most interesting parts of these reports I will mention here with their permission:

Mr. S. H. Stupakoff, Supt. Union Switch and Signal Co., writes:

"We use the acid in the proportion of two and one-half quarts to one-half barrel water, containing about twenty-five gallons," —(equal to one pound forty-eight per cent. hydrofluoric acid

in thirty-five pounds of water, the liquid would therefore contain one and four tenths per cent. HF)—" The bath is filled to the top with castings and they are left in it for about half an hour. We can renew our charge by adding each time one quart of acid.

" We find that the hydrofluoric acid is vastly superior to sulphuric acid, as the latter will not pickle satisfactorily in less than one day, and besides this we use about double the quantity of sulphuric acid compared with hydrofluoric acid to pickle the same amount of castings."—(as the quantities given by Mr. Stupakoff are by volume, this would be equal to one pound of ninety-three per cent. sulphuric acid in eleven pounds of water, the liquid would therefore contain eight and a half per cent. sulphuric acid, or six times as much as the hydrofluoric acid bath.)

"With the sulphuric acid we experienced a great deal of trouble by obtaining a white sediment on the castings, which was very difficult to remove, even when washed in hot water. This white coating would frequently work through the paint, with which the castings were subsequently covered.

" We had no occasion to try this acid for cleaning any other material but cast iron, with the exception of one instance, when we tried to remove heavy coatings of rust from a lot of mixed material, consisting of cast iron and wrought iron. The hydrofluoric acid did this to perfection and left a perfectly bright surface.

"I can say, in conclusion, that I am perfectly satisfied, that the use of hydrofluoric acid for the cleaning of new castings and corroded iron is certainly a success, and I will always prefer it to the old method of pickling in sulphuric acid."

From the engineer of another firm I received the following report:

" The best solution is one to thirty" —(this is by volume, and the bath would contain, as he used forty-eight per cent. hydrofluoric acid about two per cent. HF)—" As we make no small castings of gray iron I have only used the acid on maleable castings, with the result that small castings are cleaned excellently in two hours. I have also cleaned castings in a mixture of one acid to fifty water"—(the bath would contain about one per

cent. HF)—"by leaving them in over night, but we prefer to clean with the stronger acid. The pickling vat is usually filled up with castings three times before it requires more acid.

"It takes sulphuric acid twice as long with the same proportion"—(that is, one to thirty would give a solution of about five and six-tenths per cent. sulphuric acid)—"and then does not eat into the corners as well as hydrofluoric acid; also wastes more iron and does not leave it bright."

For iron which is to be enameled, the cleaning with hydrofluoric acid is also advantageous, because it leaves a purer metallic surface than can be obtained with other acids.

I am informed that a large firm in this city is at present making arrangements with a view of throwing out their whole mechanical cleaning plant, in which they have been cleaning sixty tons a day.

Hydrofluoric acid or its salts are also used in distilleries to insure a more complete fermentation.[1]

The latest application, of which I heard only a few days ago, is for cleaning out oil and gas wells. It seems that the shooting of a well sometimes packs the rock so tightly that the hole is dryer after the shooting than before. By pouring about six barrels of hydrofluoric acid (I suppose the acid is used diluted) into the hole, which dissolves the silicates and afterwards is pumped out again, gas or oil get an outlet.

NITROGEN ASSIMILATION IN THE COTTON PLANT.

BY CHARLES E. COATES AND W. R. DODSON.

Received March 3, 1896.

IN the spring of 1895, while looking up the literature of the cotton plant, it was noted that no quantitative work could be found touching the question of nitrogen assimilation in any member of the mallow family. As the cotton plant is highly nitrogenous in character and as there seemed to be no reason why the leguminoseae should have a prëemption claim on the absorption of free nitrogen, it was decided to undertake certain experiments along these lines, following Hellriegel's methods as far as possible, in the hope that something of importance might

[1] Article of Dr. Leo Backeland, this Journal, 14, 212.

be discovered concerning the relationships of cotton to atmospheric nitrogen. The conclusions of these experiments, however, were so entirely negative that this hope has been abandoned, and while, perhaps, they have not disproved the point in question absolutely, still it has been decided to put them on record in the belief that they afford at least strong evidence that cotton does not follow the legumes in this respect.

The method of work was as follows: A quantity of white sand was sifted through a one and a half mm. sieve, heated red hot in an iron pan and washed first with ordinary artesian water and afterwards with nitrogen-free water. Ten grams gave no nitrogen when analyzed by the usual Kjeldahl method. Ordinary flower pots were used, holding each about six pounds of sand. The sand had a water-holding capacity of about twenty-three per cent. It was kept moist to the extent of about seventy-five per cent. of its maximum capacity. The water used was obtained from artesian water nearly free from ammonia by distilling it and collecting only the middle third of the distillate. It gave merely traces of ammonia with Nessler's solution when analyzed in the usual way. A number of cotton seeds were linted as thoroughly as possible. The average weight of fifty-one seeds was 0.1166 gram. Of these, thirty-eight were weighed accurately and the weights of twenty fell between 0.110 gram and 0.130 gram. These twenty were soaked twenty-four hours in pure water, placed on moist sand in a dish, covered with a piece of filter paper, and the dish covered with a glass plate. As soon as a normal germ and rootlets appeared the seeds were planted in the pots, only those seeds being selected which showed about the same germinative energy. Before planting, four cc. of each of the following solutions were added to certain pots: potassium phosphate, 136 grams to liter; magnesium sulphate, 120 grams to liter; potassium chloride, 74.5 grams to liter; and calcium chloride, 70.8 grams to liter. The seeds were planted about three-quarters of an inch deep in the sand and the pots were covered with cotton wadding until the plant appeared. They were kept in the open air and put under cover whenever it threatened rain. On one occasion a small quantity of rain fell on the pots. Otherwise they received only nitrogen-

free water. The seeds were all planted on the first of May.

Pot 1.—No nutriment was added to this pot. The plant was dead by May 18.

Pot 2.—Same as 1. The plant was dead by May 28th.

The growths were so little in 1 and 2 that no analyses were made. To 3, 4, 5, 6, and 7 the solutions mentioned before were added. They were mixed, diluted to about 500 cc., mixed thoroughly with the sand in a porcelain dish and transferred to the pot before the seed was planted. After the plants had been growing a week or so, to 5, 6, and 7 there were added twenty-five cc. of a soil infusion, made as follows: A quantity of earth was taken from a field which had been planted in cotton for ten or twelve years. This earth was mixed thoroughly and 200 grams were shaken with one liter of water. After standing an hour or so, the clear supernatant liquid was decanted. A nitrogen determination gave 0.0002 gram nitrogen to twenty-five cc. of this liquid. It was applied by a pipette to the roots of the plant while in the pot. The assumption was that any bacterial agencies which might affect the cotton plant would surely be present in the soil of the old cotton field. A similar method had proved efficacious in innoculating legumes.

Pot 3.—With mineral food—without soil infusion. The plant died about the last of May, apparently of nitrogen starvation.

Pot 4.—Same as 3. The plant lived until the close of June, but growth had ceased by June 15. June 27 this plant and plants 5, 6, and 7, were removed from the pots and analyzed as follows: The sand was washed carefully from the roots, the entire plant was dried at 100°, and the nitrogen determined by the Kjeldahl method. In this case the seed weighed 0.1300 gram. A series of analyses had given 3.07 per cent. nitrogen in the whole cotton seed.

	Gram.
Nitrogen in seed of 4	0.004
Dry matter in seed of 4	0.5050
Nitrogen found in seed of 4	0.0068

Pot 5.—With mineral food, plus soil infusion.

	Gram.
Seed weighed	0.1244
In seed nitrogen	0.0038
Dry matter	0.4768
Nitrogen found	0.0056

Pot 6.—Same as 5.

	Gram.
Seed weighed	0.1285
In seed nitrogen	0.0039
Dry matter	0.8350
Nitrogen found	0.0074

Pot 7.—Same as 5 and 6.

	Gram.
Seed weighed	0.1175
In seed nitrogen	0.0036
Dry matter	0.9664
Nitrogen found	0.0080

In all these instances growth had stopped before the plants were removed from the pot. The gain in nitrogen without soil infusion was 0.0028 gram; with soil infusion, 0.0018, 0.0035, and 0.0044 gram. Apparently it mattered very little whether the soil infusion was added or not and in all the instances the gain was so inconsiderable as to lie well within the limits of error of the experiments. It would seem therefore that under the conditions employed the cotton plant does not assimilate atmospheric nitrogen.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 19.]

DETERMINATION OF LACTOSE IN MILKS BY DOUBLE DILUTION AND POLARIZATION.

BY H. W. WILEY AND E. E. EWELL.

Received March 20, 1896.

IN volume 6, page 289, of the *American Chemical Journal*, one of us (Wiley) published an article on the determination of lactose in milks by optical methods. The principal novelty in this process was the substitution of mercuric nitrate as the reagent for precipitating proteids in place of the other reagents which had usually been employed for that purpose. By the use of mercuric nitrate in an acid solution, it was shown in that

paper that it was possible to practically throw out all of the proteid dissolved in the milk. Inasmuch as these soluble proteids are optically active, and deflect the plane of polarization in a direction opposite to that produced by lactose, the presence of any notable quantity of them in the solution to be polarized tends to diminish the apparent percentage of lactose present. The reagent proposed, *viz.*, acid mercuric nitrate, when used in the cold and in the quantities specified, produces no inversion effect whatever upon the lactose.

In the paper referred to an arbitrary correction was made for the volume of the precipitate produced and this was fixed at two and five-tenths cc., when approximately sixty cc. of milk were used in a 100 cc. flask.

This method of estimating lactose on account of the ease with which it can be operated and its accuracy has been generally adopted by chemists. Attention has been called, however, to the fact that the arbitrary correction allowed for the volume of the precipitate is too small.[1]

Theoretically, it is evident also that the arbitrary correction admitted is too small except in cases of well-skimmed milk. In order to eliminate this arbitrary factor from the method, we undertook a series of experiments to determine the actual percentage of sugar and the proper correction to be allowed for the volume of the precipitate by the method of double dilution and polarization originally proposed by Scheibler for sugar solutions, and suggested by Bigelow and McElroy for use in the polarization of milk sugar.[2] The results of our determinations are extremely satisfactory, and show that the volume which is occupied by the precipitate in a milk varies from two and a half cc,, in the circumstances mentioned above, to six cc., according to the richness of the milk in fat. It appears, however, that this correction is less in quantity than the apparent combined volume of the fat and albuminoids which may be safely assumed to be one cc. for one gram.

All the flasks which were employed in the determinations were carefully calibrated, and the instrument used was the new triple-field shadow polariscope, made by Schmidt and

1 *Analyst*, 12, 64; 20, 126.
2 This Journal, 15, 694.

Haensch, which enables readings to be accurately made to within 0.05 per cent. All readings were made in duplicate by each of us and entered before comparisons were made, and in the polarizations given in the table the means of these four readings, which never differed by more than one-tenth per cent., are given. The polarizations were made on the contents of a 100 and a 200 cc, flask, after clarification of the milk by means of acid mercuric nitrate. In each case, double the quantity of the normal weight of milk for the instrument used was taken. The readings were calculated by the formula given by Scheibler, which requires that the reading obtained from the solution in the large flask be multiplied by two and subtracted from the reading obtained in the small flask. In all cases, in order to secure greater accuracy, our readings were made in a tube 400 mm. in length. Therefore, the data obtained in reading the solution in the small flask were divided by four in order to obtain the apparent percentage of sucrose.

The application of the formula given by Scheibler does not give absolutely accurate results. The true polarization in any given case is calculated according to the following scheme:

Let x equal the volume of the precipitate and y the correct reading. Let a equal the reading obtained from the solution in the small flask and b equal the reading of the solution from the large flask. We then have

$$200 - x : 100 - x :: a : b$$

$$200\,b - bx = 100\,a - ax$$

$$ax - bx = 100\,a - 200\,b$$

$$x = 100\,\frac{(a - 2\,b)}{a - b} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$100 - x : 100 :: y : a$$

$$100 - 100\,\frac{(a - 2\,b)}{a - b} : 100 :: y : a$$

$$100\left(a - \frac{a\,(a - 2\,b)}{a - b}\right) = 100y$$

$$y = a - \frac{a\,(a - 2b)}{a - b}$$

$$y = \frac{a^2 - ab - a^2 + 2ab}{a - b} = \frac{ab}{a - b} \ldots\ldots\ldots (2)$$

The rule derived from formula No. 2 is as follows:

The true polarization, as determined by double dilution, is found by dividing the product of the two readings made from the solutions in the large and small flasks by their difference.

In order to test the accuracy of the method, known volumes of insoluble material, as, for instance, quartz sand, were added to the flasks in order that the volume of the precipitate might be increased by a certain definite amount. The determinations were also made on the whole milk as purchased, on the same milk deprived of the most of its cream and on the cream thus secured. In all cases the results obtained were perfectly satisfactory.

Blyth has lately described a method of precipitating the casein with acid and of washing the precipitate free of sugar on a filter and polarizing the filtrate.[1] The percentage of milk sugar in the mixed filtrate and washings is about one and the polariscopic reading should be corrected for that degree of dilution. This method evidently is better suited for preparing milk whey for the gravimetric estimation of the sugar by copper, since it takes no account of the albumens still in solution and serving to a certain extent to counteract the polarizing power of the lactose.

In the presence of sucrose he proposes to estimate its quantity from the property possessed by citric acid of inverting the sucrose and leaving the lactose unchanged. Raumer and Späth[2] suggest that the polarization of milk should be preceded by boiling, since it is probable that the lactose may exhibit birotation. The data which they adduce, however, are far from convincing, since after the boiling they clear the mixture with lead subacetate and it has been shown that this reagent does not remove all the proteids. The deficit in rotation is therefore probably due to the residual soluble left-handed proteids. They further suggest that the presence of a dextrinoid body, as indicated by Ritthausen[3] may serve to increase the actual rotation of the milk sugar. In the samples which showed the apparent

1 *Analyst*, 20, 122.

2 *Ztschr. angew. Chem.*, *1896*, 72.

3 *J. prakt. Chem.* (2), 15, 348.

increase, however, they made no attempt to prove the presence of the alleged disturbing dextrin.

There seems to be no just reason, therefore, for insisting on the slow and tedious gravimetric method when a quick and accurate optical method is at hand.

Inasmuch as the time required for carrying out the method of double dilution and polarization is scarcely any longer than that required for a single polarization, it is recommended that it be done in all cases, instead of correcting the results of a single polarization by any arbitrary factor. When the determination is conducted as suggested, the analyst has at hand an easy, rapid, and accurate method of estimating milk sugar in milk, which is as desirable in all respects as any gravimetric method whatever. The data obtained are given in the accompanying table.

POLARIZATION OF MILK BY DOUBLE DILUTION.

No.	Per cent. fat.	Polarization in 200 cc. flask.	Polarization in 100 cc. flask.	Apparent per cent. lactose.	True per cent. lactose.	True volume in 100 cc. flask.	Volume of precipitate.
1	....	9.37	19.26	4.82	4.56	94.4	5.6[1]
2	....	9.59	20.33	5.08	4.54	88.8	11.6[2]
3	....	9.36	19.20	4.80	4.57	95.0	5.0[3]
4	....	9.60	20.25	5.06	4.56	89.7	10.3[4]
5	2.9	10.15	20.84	5.21	4.95	94.8	5.2
6	4.8	10.31	21.21	5.30	5.00	94.5	5.5
7	3.1	9.49	19.41	4.85	4.64	95.7	4.3[5]
8	4.0	10.01	20.45	5.11	4.90	95.9	4.1
9	1.4	9.44	19.26	4.82	4.63	96.1	3.9[6]
10	5.5	11.05	22.68	5.67	5.38	94.8	5.2
11	4.4	9.57	19.47	4.87	4.71	96.5	3.5[7]
12	2.0	9.75	19.93	4.98	4.77	95.8	4.2[8]
13	17.6	8.72	19.13	4.78	4.01	82.4	17.6[9]

Summary of Method.—For the scale of the instrument used, 32.91 grams of pure lactose in 100 cc. give a reading of 100. This number is derived from the following data: For sucrose concentration twenty-five grams in 100 cc., $[\alpha]_D^{20°}=66.37$.

1 Without sand.
2 With five cc. quartz sand.
3 Without sand.
4 With five cc. quartz sand.
5 Same as No. 6, after separation of cream.
6 Same as No. 8, after separation of cream.
7 Whole milk.
8 Skimmed milk.
9 Cream.

For lactose, thirty-three grams in 100 cc., $[\alpha]_D^{20°} = 52.53$. ; then $66.37 : 52.53 :: x : 26.048$, whence $x = 32.91$. The temperature of the working room should be kept at about 20°, since the rotatory power of lactose diminishes in a small degree as the temperature rises. Double the quantity mentioned, *viz*,, 65.82 grams of milk are placed in a 100 cc. flask, clarified with mercuric nitrate solution, the volume completed to the mark, the contents of the flask well shaken, poured upon a filter, and the filtrate polarized in a 400 mm. tube. A similar quantity of the milk is placed in a 200 cc. flask and subjected to the same treatment. The polarimetric data obtained are used for calculating the true volume of liquid in the flask and the true percentage of lactose and the true volume occupied by the precipitate, in accordance with the rule already given, or with sufficient accuracy by Scheibler's formula. The acid mercuric nitrate solution is prepared as follows :

Dissolve mercury in double its weight of nitric acid, specific gravity 1.42, and add to the solution five volumes of water. This solution is more dilute than the one recommended in the original paper, it having been noticed that a stronger solution colors the precipitated proteid matter slightly yellow (xanthoproteic reaction). Ten cc. of the reagent are to be employed instead of two, as directed for the stronger solution. In preparing the solution of milk in the 200 cc. flask it may be necessary at times to use more than this quantity of the acid mercuric nitrate in order to secure a filtrate entirely free of turbidity.

An inspection of the data in the table shows a general agreement between the volume of the precipitate found and the percentage of fat in the sample with the exception of one instance, *viz.*, No. 11. It is evident that in solutions so dilute, a slight variation in the volume has a very small influence on the percentage of sugar found. An error of 0.05 degree in the reading of the dilute solution (200 cc. flask) makes an error of 0.05 per cent. in the result. The error due to one cc. of the precipitate in the dilute solution is approximately 0.05 per cent. It is therefore evident that with proper care the percentage of sugar can be determined to within one-tenth per cent. by the polarimetric method and this is entirely sufficient for all practical purposes.

[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM. No. 5.]

A STUDY OF THE ZIRCONATES.

By F. P. Venable and Thomas Clarke.

Received March 6, 1896.

THIS class of compounds of zirconium has received but little attention from chemists. The chief investigator in the past who has worked in this field was Hiortdahl.[1] Of recent years several papers by L. Ouvrard[2] have appeared. The accounts given in the various text books of these zirconates are based upon the work of Hiortdahl or upon such abstracts of it as were to be found in the Jahresberichte, or in such dictionaries as that of Watts. This is unfortunate, as to the best of our knowledge the work of Hiortdahl itself is in some respects inaccurate and erroneous, and the abstracts of it are misleading. Before giving an account of our own experiments, it may be well to gather together the statements regarding these bodies as given by Watt and in the original article of Hiortdahl.

Watts says that the compounds of zirconia with the stronger bases are obtained by precipitating a zirconium salt with potash or soda, also by igniting zirconia with an alkaline hydroxide. "Zirconate of potassium thus obtained, dissolves completely in water." His first mode of preparing the zirconates is very questionable; the last statement is not true. He then goes on and describes zirconates of sodium, calcium and magnesium, as described by Hiortdahl. The details of Hiortdahl's analyses, etc., will show on what an imperfect basis the knowledge of the constitution of these bodies rests. Hiortdahl states that he secured direct union only by ignition with alkaline carbonates. His attempts with the volatile chlorides failed. On heating zirconia with sodium carbonate one equivalent of carbon dioxide was driven out, and it is on the loss of carbon dioxide upon ignition that his figures for the composition of the resulting products are largely based. On heating equivalent amounts of zirconia and sodium carbonate a crystalline mass was obtained, which slowly absorbed moisture from the air. On treating this with water no decomposition was noted at first, but soon the water became alkaline and zirconia separated. This was taken as proof

[1] *Ann. Chem. Pharm.*, 137, 34, 236.

[2] *Compt. Rend.*, 112, 1444–46, and 113, 1021–22.

that the zirconia was decomposed by the water. In the experiment 0.3910 gram zirconia heated with 0.3130 gram sodium carbonate to a dark redness for nine hours lost 0.1310 gram carbon dioxide, and on treatment with water 0.3871 gram "zirconia," or 99.03 per cent. was left. If an excess of sodium carbonate is used one can drive out two equivalents of carbon dioxide. A little further down he notes that the "Gewichtsverlust zugleich von der Temperatur und der Dauer des Glühens abhängt." These are the determinations from which formulas for the zirconates are worked out.

It is scarcely necessary to say that for purposes of calculation these figures are entirely worthless. The loss of carbon dioxide is due to a partial formation of hydroxide as well as to a combination with zirconia. The fused mass of sodium carbonate, hydroxide, zirconate and unchanged zirconia will of course prove hygroscopic, and water will wash away all except the last two mentioned. We have failed to get any positive evidence that a zirconate formed by fusion was decomposed by water or was appreciably soluble in it.

In his second paper, Hiortdahl treats the fused mass of zirconia and sodium carbonate with water acidified with hydrochloric acid and analyzes the residue, finding in it: ZrO_2, 78.54 per cent.; Na_2O, 5.40 per cent.; and H_2O, 16.89 per cent., corresponding to $Na_2O.8ZrO_2$. He gets the zirconate of magnesium and calcium by fusing zirconia and silica with magnesium chloride and calcium chloride respectively.

Ouvrard obtained his zirconates by fusions with the chlorides, also using those of lithium, calcium, strontium and barium. In some cases, instead of using zirconia, he took powdered zircons, obtaining silico-zirconates.

In our own experiments the following methods of forming the zirconates were tried:

I. Fusing in boron trioxide, the zirconia and the basic oxide (Ebelmen).

II. Fusing zirconia with alkaline carbonates, (Hiortdahl).

III. Fusing zirconia with alkaline hydroxides.

IV. Fusing zirconia with alkaline or earthy chlorides (Hiortdahl).

V. Precipitation of solutions of zirconium salts with alkaline hydroxides (Watts).

VI. Dissolving zirconium hydroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralization with an acid.

I. FUSION WITH BORON TRIOXIDE.

This method, made use of by Ebelmen in the case of other oxides, is useless in the case of zirconia, because this oxide is not taken up by the boron trioxide, and so does not come in contact with the other oxide. The melt of boron trioxide was kept at a high temperature for a number of hours without any appreciable solvent action upon the zirconia, added in small portions.

II. FUSION OF ZIRCONIA WITH ALKALINE CARBONATES.

The purified zirconia used had been dried at the temperature of the steam bath and therefore was not in the inactive condition brought about by igniting it at a very high temperature. This was the case in the subsequent experiments also.

It is by fusion with sodium carbonate that Hiortdahl claimed to have prepared his ziconates. Ouvrard seems to have gotten little besides crystals of zirconia. Very little action could be seen in the experiments described below. The zirconia sank to the bottom of the fused mass and remained without apparent change for hours. Varying the time of heating did not seem to have much effect upon the results.

After the fused mass had cooled it was leached with successive portions of water until no alkali could be detected. The wash water contained no zirconium. As the mass left will absorb carbon dioxide, it was dried as rapidly as possible at about 150° to constant weight. Dilute hydrochloric acid was used to separate the zirconate formed from the unchanged zirconia. As this zirconia was now in the ignited and even crystalline form, it was concluded that it was insoluble in the dilute acid. The zirconia in the solution was precipitated as hydroxide and determined as oxide, and the alkali determined in the filtrate. Two grams of zirconia were used in each case and a large excess of the carbonate. The amount of unattacked zirconia ranged from ninety-

three to ninety-nine per cent., showing thus very little action after many hours of fusion. In some cases, therefore, the amount of supposed zirconate obtained was too small for reliable analysis.

I. WITH SODIUM CARBONATE.

Three experiments with sodium carbonate were carried to completion.

1. Two grams zirconia and eight grams sodium carbonate were fused three hours. Amount of residue after leaching, soluble in dilute hydrochloric acid, 0.1588 gram, or eight per cent. In this $ZrO_2 = 75.70$ per cent.; $Na_2O = 24.30$.

2. Two grams zirconia fused with sixteen grams sodium carbonate for four hours. Amount of residue soluble in hydrochloric acid, 0.3042 grams. Percentages: ZrO_2, 74.18; Na_2O, 25.81. These correspond fairly with $(ZrO_2)_3(Na_2O)_2$.

3. Two grams zirconia fused with sixteen grams sodium carbonate for eight hours. Amount soluble in dilute hydrochloric acid 0.1220 gram, or six per cent. Percentages: ZrO_2, 58.16; Na_2O, 41.84.

II. WITH POTASSIUM CARBONATE.

When potassium carbonate was used the action was so slight that it was not possible to get enough for analysis. In one case, after heating for ten hours, the amount soluble was just one-half per cent. This accords with the observation of Ouvrard.

Of course it is possible that the leaching with water had a partially decomposing effect upon the zirconates. Very little could be justly concluded, however, from experiments in which there was so little action, therefore the effort at forming the zirconates by fusion with the carbonates was abandoned.

III. FUSION OF ZIRCONIA WITH HYDROXIDES.

1. Fusion with sodium hydroxide.

Here considerable action was noticed. The fusions were made in a silver dish. The heating was kept up until the mass became semi-solid. The treatment of the fused mass and the analysis were carried out as before. No zirconium was detected in the wash water.

1. Two grams zirconia fused with eight grams sodium hydroxide. Total amount dissolved 1.1855 grams. An analysis, reduced to dry basis, gave ZrO_2, 92.29, and Na_2O, 7.65.

2. Same amount taken as in Experiment 1. Total amount dissolved 0.7655 gram, containing ZrO_2, 93.19, and Na_2O, 6.22.

3. Two grams zirconia and sixteen grams sodium hydroxide. Amount dissolved 0.8004 gram, containing ZrO_2, 92.57, and Na_2O, 7.38.

4. Two grams zirconia were fused with eight grams of sodium dioxide, instead of the hydroxide. Amount dissolved 0.7074 gram, and this contained 91.21 per cent. ZrO_2.

$Na_2O.(ZrO_2)_6$ contains ZrO_2, 92.20; and Na_2O, 7.80.

$Na_2O.(ZrO_2)_7$ contains ZrO_2, 93.29; and Na_2O, 6.76.

2. Fusion with potassium hydroxide.

These were carried out in a manner similar to those with sodium hydroxide and the action seemed to be about the same. In each experiment two grams of zirconia were taken and fused with sixteen grams of potassium hydroxide.

1. Dissolved by hydrochloric acid 0.8850 gram which contained 79.63 per cent. ZrO_2.

2. Dissolved 1.5241 grams which contained ZrO_2, 82.98; K_2O, 17.00.

3. Dissolved 1.2078 grams which contained ZrO_2, 78.59; K_2O, 21.40.

4. Dissolved 0.9297 gram which contained ZrO_2, 85.51; K_2O, 14.49.

In analyzing these alkaline zirconates the water present was not determined. The moist powder was treated with hydrochloric acid, the insoluble portion caught upon a filter, and the zirconia and alkali determined in the filtrate and the results calculated upon a dry basis. If the analysis given by Hiortdahl is calculated upon a dry basis, it gives for ZrO_2, 93.51, and Na_2O, 6.49, or very nearly the numbers gotten in Experiment 2 in the fusions with sodium hydroxide.

It is difficult to interpret the results of these fusions with the alkaline carbonates and hydroxides. The fusions do not yield the same definite results each time, and indeed it can not be claimed from the analyses that definite zirconates have been pre-

pared. Some allowance must be made for the imperfect method of separation of the zirconate from the unchanged zirconia, some of the former being taken up by prolonged digestion with hydrochloric acid. There is a marked tendency, however, toward the formation of certain zirconates under approximately the same conditions. Two of the experiments with sodium carbonate give results fairly in accordance with the formula $(Na_2O)_2(ZrO_2)_3$. In the fusion with sodium hydroxide the results range from $(Na_2O)(ZrO)_5$ [$ZrO_2 = 90.76$; $Na_2O = 9.24$], to $(Na_2O)(ZrO)_8$ [$ZrO_2 = 94.08$; $Na_2O = 5.92$], and it is with these that the analysis of Hiortdahl agrees, though his was a fusion with sodium carbonate. Why there should be this difference is not very clear. The tendency is manifestly toward the formation of what may be called the polyzirconates, having a considerable excess of zirconic acid. In the case of potassium the carbonate failed to give a compound. The hydroxide gives results ranging from $(K_2O)(ZrO_2)_3$ [$ZrO_2 = 79.57$; $K_2O = 20.43$], to $(ZrO_2)_5(K_2O)$, [$ZrO_2 = 86.74$; $K_2O = 13.26$]; again polyzirconates with excess of zirconia.

Other fusions were carried out with sodium and potassium hydroxides, and the resulting masses were leached with dilute acetic acid, a solvent which had to be used in leaching away the alkaline earths in the subsequent experiments. In the case of sodium the leaching removed practically all of the alkali. In the case of potassium a substance containing ZrO_2, 78.59 per cent., and K_2O, 21.41 per cent. was left. This nearly corresponds to the formula $K_2O.(ZrO_2)_3$. It is almost exactly the result gotten in one of the previous experiments.

3. Lithium gave no zirconate when the carbonate was used for the fusion. With the hydroxide it gave the following results:

Two grams ZrO_2 were fused with excess of lithium hydroxide, leached with dilute acetic acid and with water. This gave on analysis ZrO_2, 89.11 per cent.; Li_2O, 10.99 per cent. Percentage of ZrO_2 calculated for $Li_2O.2ZrO_2$ is 89.13.

4. Calcium oxide was also heated for a number of hours with zirconia and gave the following results:

	I.	II.	Calculated for $CaO.ZrO_2$.
ZrO_2	70.11	70.83	68.54
CaO	29.88	29.14	31.46

These residues, after treatment with dilute acetic acid and water, were crystalline.

5. Barium hydroxide differs from that of calcium in that it fuses readily and thus affords much better opportunity for reaction. The fusion gave abundant evidence of action. The excess of hydroxide was washed out with water. The carbonate present was dissolved away with dilute acetic acid until there was no more barium in the wash water. No zirconia was found in any of these washings. Towards the latter part of the washing the solid particles settled out with great difficulty. The residue was analyzed with the following result:

	Found.	Calculated for $BaO.ZrO_2$.
ZrO_2	55.51	55.95
BaO	44.49	44.05

This is a grayish white powder, very fine and easily soluble in hydrochloric acid. Practically all of the zirconia was taken up, leaving little undissolved by the hydrochloric acid.

6. Strontium oxide was prepared by ignition of the nitrate and heated in the same way as the calcium oxide. This mass was pinkish white, probably from slight impurities, and was completely soluble in dilute hydrochloric acid. On analysis the following results were obtained:

	Found.	Calculated for $SrOZrO_2$.
ZrO_2	54.22	54.55
SrO	45.77	45.45

7. The magnesia (eight grams) and zirconia (two grams) was heated together for about four hours and then treated in the same manner as the calcium fusion, *i. e.*, first leached with dilute acetic acid and then washed with water until free from magnesia. The residue gave evidence of being crystalline.

	Found.	Calculated for $MgO.ZrO_2$.
ZrO_2	76.28	75.30
MgO	23.70	24.70

IV. FUSION OF ZIRCONIA WITH CHLORIDES.

This method was used by Hiortdahl in preparing the zirconates of magnesium and calcium, and by Ouvrard for the same, and also for strontium, barium and lithium. According to the latter they all gave zirconates of the form M_2ZrO_3.

1. Fusion with sodium chloride.

There appeared to be very little action. The fusion was washed with water until free from chlorine. It was then treated as in the case of the carbonates. When two grams of zirconia were fused with sixteen grams of sodium chloride, it was found that less than two per cent. had been dissolved. In a second experiment, after heating six hours, the amount dissolved was less than two-tenths of a per cent.

2. Fusion with potassium chloride.

No action was observable. When two grams of zirconia were heated a number of hours with an excess of potassium chloride and the mass then treated as above, only three-tenths of a gram had been acted upon. There seemed to be even less action in the case of lithium chloride at the temperature attainable by means of an ordinary water-blast lamp.

3. Fusion with alkaline earths.

Two attempts were made to prepare magnesium zirconate by fusing zirconia with magnesium chloride and ammonium chloride. It was not possible to prevent decomposition of the magnesium chloride. There seemed to be some action, but much difficulty was experienced in separating the products. The method described by Ouvrard gave evidences of zirconium in the washings.

In the case of fusions with calcium chloride no action could be observed. Two experiments were made, following closely the directions of Ouvrard, except as to temperature possibly, as to which no exact directions were given. A water-blast lamp was used for several hours. After leaching and washing, the mass left behind gave no zirconium to hydrochloric acid.

Our experiments with the chlorides have led us to believe that there is little or no action between zirconia and the chlorides of the alkalies or alkaline earths except where these chlorides are

decomposed by the heat and oxides formed. Any action noticed is to be attributed to the oxides.

V. PRECIPITATION FROM THE SOLUTION OF A ZIRCONIUM SALT BY MEANS OF AN ALKALINE HYDROXIDE.

Watts speaks of this method but no experiments are recorded. It seemed to us upon examination of the question that very little evidence as to the existence of the zirconates or their properties could be drawn from such a method of preparation as this. It has been repeatedly observed that the precipitate formed by means of ammonium hydroxide is extremely hard to wash free from ammonia. After a very large number of washings, however, it is practically free from ammonia. The same is true of sodium and potassium hydroxides. Is it to be inferred that a definite zirconate is precipitated? At what point shall the washing be stopped, for manifestly some washing is necessary? Equally it cannot be decided because of this loss of alkali by prolonged washing, that we have a decomposition of the zirconate caused by the action of the water. It, therefore, seemed to be quite useless to make analyses of the precipitates gotten with different degrees of washing; especially as somewhat similar experiments were carried out under the next heading.

VI. THE SOLUTION OF ZIRCONIUM HYDROXIDE IN CAUSTIC ALKALI.

It was found that zirconium hydroxide was perceptibly soluble in solutions of potassium and sodium hydroxide. Experiments were first made with a view of determining the extent of this solubility. Solutions of the two alkalies were made up of different strengths, an excess of zirconium hydroxide added, and the solution then boiled. After cooling, a measured quantity of the solution was drawn off and the amount of zirconia present determined.

A 50	per cent	solution	potassium	hydroxide	dissolved	per	cc.	0.00233	gram.
33	"	"	"	"	"	"	"	0.00097	"
25	"	"	"	"	"	"	"	0.00075	"
12	"	"	"	"	"	"	"	0.00009	"

In the case of sodium hydroxide there seemed to be a stronger solvent action.

A 33 per cent solution dissolves per cc. 0.00245 gram.						
25	"	"	"	"	" 0.0012	"
12	"	"	"	"	" 0.0005	"

If a concentrated solution of alkali, saturated with zirconium hydroxide, is diluted, a portion of the zirconium will be precipitated. Neutralization with acid will also cause a precipitation of the zirconium. In both cases alkali is retained by the precipitate in spite of washing. Analyses were made of some of these precipitates after very thorough washing (in no case was less than a liter of water used.) The results in four experiments were sufficient to show that these precipitates were practically zirconium hydroxide with a varying percentage of alkali, this percentage ranging from 1.15 to 3.94. It is possible to assume that zirconates were formed and then decomposed by the action of the water during the washing, but it seems more probable that this is, as is true in the case of so many hydroxides precipitated by alkaline hydroxides, merely a stubborn retention of alkali. Assuming that the strong alkaline solutions held zirconates in solution, attempts were next made to prepare other zirconates by precipitation from them.

The addition of solutions of various salts gave small precipitates which seemed to be formed mainly because of the dilution of the alkaline hydroxide and to consist almost entirely of zirconium hydroxide. It was necessary, therefore, to use strongly alkaline solutions of the compounds of the elements to be experimented with. This greatly diminished the choice of compounds. Concentrated solutions of aluminum and zinc hydroxides in potassium hydroxide gave precipitates but they were in too small amounts for reliable analyses to be made.

Summing up the results of the experiments performed, it is clear that the method yielding the best results for the preparation of the zirconates is fusion of gently dried zirconia with hydroxides or prolonged heating with the oxides. In the case of the alkaline earths this yields zirconates containing one equivalent of each oxide, as CaO.ZrO, etc. The same is true of the magnesium compound. For lithium the compound obtained was LiO.ZrO. For the alkalies it seemed to be possible to ob-

tain only zirconates having a largely preponderating proportion of zirconia. There seems to be a tendency toward the formation of distinct compounds under certain conditions. These polyzirconates, and the lithium compound also, may be decomposition products due to the action of the water used in leaching. No other mode of separation from the products of the fusion could be devised by us, however. If they are produced by the decomposing and solvent action of the water, it is a little strange that a point should be reached beyond which the leaching extracted no more alkali, and that this point varied with changed conditions. This is not the case where zirconium hydroxide has been precipitated by an alkali.

DOUBLE ZIRCONATES.

Two attempts at the formation of double zirconates were made.

1. Potassium calcium zirconate.

About two grams each of zirconia, potassium hydroxide and lime were heated together for about four hours. There was evidence of considerable action. The mass was treated with dilute acetic acid and thoroughly washed. Then on treatment with dilute hydrochloric acid nearly the whole residue went into solution. The analysis gave ZrO_2, 67.21 per cent.; CaO, 31.06; K_2O, 1.11. This is a calcium zirconate, ($CaO.ZrO_2$), with a small part of the CaO substituted by K_2O.

2. Potassium aluminum zirconate.

Two grams of zirconia were fused for eight hours with two grams of potassium hydroxide and three grams of alumina. The mass was washed with dilute acetic acid until no more alumina was dissolved. The residue was treated with dilute hydrochloric acid and the insoluble portion removed by filtration. The analysis gave ZrO_2, 72.38 per cent.; Al_2O_3, 7.66; K_2O, 20.00. These experiments indicate the possible existence of double zirconates, and when time admits this point will be further examined.

UNIVERSITY OF NORTH CAROLINA.

A MODIFIED AMMONIUM MOLYBDATE SOLUTION.

BY A. L. WINTON.

Received March 18, 1896.

WHEN phosphoric acid is determined by the molybdate method, it is a common practice to add fifteen grams of ammonium nitrate to the phosphate solution and heat before adding ammonium molybdate. By this means the separation of the yellow precipitate is greatly facilitated and the time of digestion shortened. But to dissolve this nitrate requires some time and very greatly reduces the temperature of the solution so that special care is necessary in heating it subsequently. In the laboratory of this station it has been our practice to simplify the process by omitting the separate addition of ammonium nitrate and using a molybdic solution containing the requisite quantity of the salt. Such a solution may be prepared according to the following formula:

I. Dissolve 1000 grams of molybdic acid in 4160 cc. of a mixture of one part of concentrated ammonia water (sp. gr. 0.90) and two of water.

II. Dissolve 5300 grams of ammonium nitrate in a mixture of 6250 cc. of concentrated nitric acid (sp. gr. 1.4) and 3090 cc. of water.

Add I to II slowly with constant stirring. Allow to stand for a few days in a warm place and decant off the clear liquid.

This solution has the same proportion of ammonium molybdate and free nitric acid as the molybdic solution of Fresenius, but differs from the latter in that *fifty cc. contain fifteen grams more of ammonium nitrate*. We have prepared the solution so as to contain this proportion of the salt because in the routine analysis of fertilizers in the station laboratory fifty cc. are most commonly employed. This quantity in our experience is usually sufficient for the precipitation of the soluble, insoluble or total phosphoric acid of mixed fertilizers in solutions representing four-tenths, two, and five-tenths grams respectively of the material.

In no case ought less than fifty cc. be used, for otherwise there may not be enough ammonium nitrate present for the perfect separation of the yellow precipitate. When a larger quan-

tity of molybdic solution is required, as, for example, in the determination of total phosphoric acid in ground bone, bone black, Thomas slag, etc., it may be added without fear that the larger quantity of ammonium nitrate contained in it will in any way interfere with the process. If, however, it is thought desirable, a special molybdic solution containing fifteen grams of added ammonium nitrate to every seventy-five or 100 cc. of the liquid may be prepared for such cases.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION,
NEW HAVEN, CONN.

ON THE ESTIMATION OF SULPHUR IN PYRITES.

BY THOMAS S. GLADDING.
Received March 30, 1896.

IN the October (1895) number of this Journal, Dr. Lunge continues his discussion of the estimation of sulphur in pyrites. He presents no new experimental support of his position. He indirectly accuses me of having published a "private" communication without the sanction of the writer, Prof. Richards. In reply I will say that the words of Prof. Richards were published by myself, not only with full permission, but after a careful revision of the same by their author. Had Dr. Lunge addressed a note to Prof. Richards or to myself, he would have been saved from making a most unkind and needless accusation.

While Lunge attempts no further support of his position by chemical experiment, he makes the claim that any occlusion of barium chloride that occurs is compensated for by the solubility of barium sulphate in the acid liquor of precipitation. In his own words "my claim has been that my method by compensation of unavoidable errors, gives *correct results*."

I have investigated this claim of Lunge's, as far as it applies to the occlusion of barium chloride in his method, in the following manner: I have had one of our assistants repeat the work with chemically pure sulphate of ammonia, using two grams in each case, making comparison precipitations with a ten per cent. solution of barium chloride, the first by adding the barium chloride solution drop by drop from a burette, the second by sudden addition from a small beaker in which it had been brought to the boiling point. The results were as follows:

	By slow addition. Gram.	By sudden addition Gram.
Sulphur	0.4840	0.4880
Sulphur	0.4820	0.4873

These experiments show an occlusion of about 0.040 gram barium chloride and a corresponding error of 0.50 to 0.55 per cent. in the estimation of the sulphur present.

I repeated personally the second series of precipitations obtaining:

	Barium sulphate obtained. Grams.	Sulphur. Gram.
1	3.5480	0.4878
2	3.5430	0.4871

These experiments show an error of about 0.55 per cent. in the estimation of sulphur present. The greatest care was taken in washing these precipitates. Three washings by decantation, using seventy-five cc. of hot water each time, were followed by five washings on the filter paper.

I now fused these precipitates with chemically pure sodium carbonate, dissolved the flux in water, filtered from barium carbonate, acidified the filtrate with nitric acid, added silver nitrate and from the silver chloride obtained, calculated the equivalent of barium chloride. I obtained in one case 0.0552 gram silver chloride, corresponding to 0.040 gram barium chloride, in the other 0.0500 gram silver chloride, equivalent to 0.0364 gram barium chloride. Deducting these figures, we have:

$BaSO_4$	3.5480	3.5430
$BaCl_2$	0.0400	0.0364
Pure $BaSO_4$ obtained	3.5080	3.5066

The sulphur obtained from these corrected results are 0.4823 gram and 0.4821 gram. These corrected results agree very closely with those obtained by our assistant when using the dropping method. I now fused one of the precipitates obtained by the dropping method with sodium carbonate in the same way and obtained 0.0027 gram silver chloride, equivalent to 0.002 gram barium chloride. This shows that the occlusion of barium chloride is practically avoided by adding the barium chloride drop by drop, as 0.002 gram barium chloride would cause an error of only 0.026 per cent. in sulphur.

I now took up the question of the solubility of barium sulphate in the acid liquor of precipitation, imitating the conditions under which the actual analysis of pyrites is made. To 400 cc. water were added fifteen cc. strong ammonia. Hydrochloric acid was now added to acidify. To two such preparations I added 0.020 gram and 0.040 gram chemically pure ammonium sulphate, respectively. The solutions were brought to the boiling point and ten cc. barium chloride added. The liquid was boiled till clear and allowed to settle. I obtained :

	Barium sulphate. Gram.	Sulphur obtained. Gram.	Sulphur present. Gram.
1	0.034	0.00468	0.00484
2	0.069	0.00949	0.00969

The sulphur lost by the solubility of the barium sulphate in the acid solution in the above experiments amounts to 0.016 and 0.020 per cent. respectively.

The above work demonstrates conclusively that the method employed by Lunge of adding the barium chloride all at once causes an error of about five-tenths per cent. in the percentage of sulphur, and that such error is *not* compensated for by the solubility of barium sulphate in the liquor of precipitation, as such solubility is very slight, causing an error of less than 0.03 per cent.

In his first reply (March, 1895), Dr. Lunge objected to my method of estimating the 0.20 to 0.40 per cent. of sulphur, (that may be left in the ferric hydroxide), by the simple process of dissolving the latter in dilute hot hydrochloric acid, adding ten cc. of barium sulphate solution and letting stand over night. This he declared was wrong, owing to the solubility of barium sulphate in such solution. I showed by a few simple and rigid experiments that I was entirely right. These experiments were very easily capable of repetition. But Lunge did not choose to repeat them. The above experiments showing that the sudden addition of barium chloride will cause an error of several tenths of a per cent. are likewise very easily repeated and the separation of the occluded barium chloride as described, is so positive as to the error caused by Lunge's method of procedure, that I hope for a further answer from Dr. Lunge. On account

of the commercial importance of an accurate estimation of sulphur in pyrites, I have no doubt that a prompt repetition of my work as described above will soon be published by some other analyst, and the main point at issue, namely, the necessity of a very slow addition of the barium chloride solution, be settled.

FURTHER NOTES UPON THE FATS CONTAINED IN THE TUBERCULOSIS BACILLI.

By E. A. de Schweinitz and Marion Dorset.

Received March 28, 1896.

In the *Journal of the American Chemical Society*, for August, 1895, we published an article upon the composition of the tuberculosis and glanders bacilli, and noted the probable composition of the fats which are present in these germs in considerable proportion. The amount of crude fat in the tuberculosis bacilli is very large, having been found by us to be in round numbers thirty-seven per cent. of the weight of the dried germs. In the article referred to the amount of fat at our disposal was very small, and we could at that time determine only palmitic acid, and a high melting acid, which we stated appeared to be arachidic so far as the quantity at hand could be utilized. Recently we have made some further study upon these fats, and the results so far obtained seem to be of sufficient interest to warrant publication as a continuation of our previous work.

The quantity of crude fat available, which had been extracted from the germs was about three and five-tenths grams, and this was examined in the following way: It was first saponified in a closed flask with sodium hydroxide, in accordance with the method prescribed, for the determination of fats by the American Association of Official Agricultural Chemists, as this method seemed to give the most satisfactory results. The saponification yielded a hard soap which was difficultly soluble in water. The dissolved soap was acidified with sulphuric acid and submitted to distillation until 100 cc. of the distillate had been obtained, again in accordance with the usually prescribed method. The distillate had a pungent odor, something like that of sweet almonds, and when titrated with tenth normal hydroxide

solution, required for neutralization two and four-tenths cc. of the latter. The total amount of volatile fatty acid was therefore exceedingly small. As the total amount of sodium hydroxide required to neutralize the volatile acid from three and five-tenths grams fat was only 0.0096 gram, the total quantity of volatile acid could probably not have been 0.05 gram, an amount too small to permit of a determination of its character.

The non-volatile fatty acids which formed a hard layer in the distilling flask were filtered off and well washed with water to remove all sulphuric acids and salts. The mixture was partially soluble in cold ninety-five per cent. alcohol, but readily soluble in hot absolute alcohol. The only method that appeared practical for the separation of the fatty acids in this mixture, was a fractional crystallization. Even this was extremely troublesome, but finally by repeated efforts the larger portion of the acid was found to have a melting-point of 62° C., which remained constant upon recrystallization. The principal fatty acid was therefore palmitic. After the palmitic acid had been removed a residue remained which was partially soluble in cold eighty-five per cent. alcohol, and partially in hot eighty-five per cent. alcohol. The acid soluble in hot eighty-five per cent. alcohol after the first crystallization melted at 85° C., while two subsequent crystallizations raised the melting point to 102° C. Unfortunately again the quantity of this high melting acid was too small for further crystallization or identification. It was evidently the same acid that in our first article we noted as probably arachidic acid.

The acid soluble in cold eighty-five per cent. alcohol was further purified and gave white crystals that melted at 42°–43° C., which would correspond to lauric acid. The amount was too small to permit of a positive identification.

This examination of the tuberculosis fats has shown that it is principally a glyceride of palmitic acid. In addition there is a minute amount of the glyceride of a volatile fatty acid to which the tuberculosis cultures owe their characteristic odor, and very small amounts of probably lauric acid and an unusually high melting acid, an acid apparently with a larger carbon content, so far as we can find, than any before noted in plants.

We propose still to identify the volatile and non-volatile acids found in such small quantities, but as it will require probably several years to collect the material for this work, it has seemed best to give the results so far obtained at the present time.

THE CASSEL-HINMAN GOLD AND BROMINE PROCESS.

BY PARKER C. MCILHINEY.

Received March 24, 1896.

THIS process, recently introduced by the Gold & Bromine Co., is for the extraction of gold from low grade ores, and those which will not give up their gold to amalgamation. If an ore is free milling no process yet devised can compete with amalgamation for its treatment, and if it is of sufficiently high grade to bear transportation and smelting charges, and contains nothing to interfere with the process of smelting, there is comparatively little inducement to use a wet process. But for ores such as the telluride ores of Colorado, which will not amalgamate, and in which the gold and tellurium compounds are of such a friable nature that they cannot be concentrated, and which are in addition of too low grade to smelt, some wet process must be used. The wet processes which have proved commercially successful are chlorination and the cyanide process. Of the cyanide process nothing need be said except that on many ores it has been used very successfully and from many others it fails to extract a sufficiently high percentage of the gold present. Chlorination has, after being the subject of a great deal of experimenting, been reduced practically to two methods of operation: the vat process, in which the ore is treated with chlorine gas and water, without agitation, and the Thies barrel process, in which the ore is agitated in a revolving barrel with water, bleaching powder, and oil of vitrol. Of the two the barrel process is more generally applicable as the ore cannot be leached in vats unless it is comparatively free from slime and allows the liquid to pass through it readily. The barrel process is recognized generally as better practice. It is evident that in the vat process the strongest solution of chlorine which can at any time be in contact with the ore will be an aqueous solution saturated at the ordinary temperature and pressure, because it

is impracticable to place the vats under pressure. In the barrel process it has also been found impracticable, on account of mechanical difficulties, to treat the ore with chlorine under any considerable pressure, and, therefore, in the Thies process the strength of the chlorine solution is almost as limited as in the vat process, and moreover it has been found impracticable to introduce the chlorine in the Thies process as free chlorine, and it is now made entirely by means of bleaching powder and oil of vitriol, introduced with the ore. In order to effect the solution of the gold in the ore in a reasonably short time it is not sufficient to introduce a *small* excess of chlorine but a very large excess must be used to so hasten the solution as to bring the time within permissible limits. This excess of chlorine goes to waste, and although very many attempts have been made to recover it, none have ever proved practicable. The only safe way to get the gold out is to use as large an excess of chlorine as possible, and as the solubility of chlorine in water prevents the use of more than a small amount, it sometimes happens, even with careful working, that the ore being improperly roasted no gold is obtained at all.

As a substitute for chlorine, bromine has been used by many experimenters, and its use has been attempted in mills by a simple substitution of bromine for chlorine. But as bromine is very expensive its use without recovery has not been successful.

The properties of the two halogens, as far as concerns their use on ores, are about as follows:

Bromine is, at ordinary temperature, a liquid, boiling at 63° C., and which may be easily liquified again by a condenser supplied with cold water.

Chlorine is a gas which must, according to Nieman,[1] be placed under a pressure of six atmospheres at 0° C. in order to liquefy it, or cooled to —35° C. to condense it without pressure.

Bromine is soluble in water at 15° C. to the extent of three and two tenths per cent; this means about 25.5 pounds in 100 gallons of water.

Chlorine is soluble in water to the extent of about 0.76 per

[1] Brandes Arch., 36, 18; Dammer, Handb. Anorg. Chem., I, 474.

cent. at 15° C.; this means about six pounds in 100 gallons of water.

Bromine is a much less powerful oxidizing agent than chlorine, and, as a result of this fact, oxidizable materials such as pyrites are much less acted upon by bromine than by chlorine. In fact it is possible to treat with bromine water pyrites containing gold and extract most of the gold as bromide without attacking much pyrites, which it is not possible to do with chlorine water.

Bromine dissolves gold more easily than chlorine. The experiments made by T. K. Rose, at the Royal Mint in England, recorded in his "Metallurgy of Gold," page 242, show that a saturated solution of chlorine in water, that is about 0.76 per cent. of chlorine, dissolved 57.6 parts of gold, while a two-tenths per cent. solution of bromine in water, less than one-third the strength of the chlorine, dissolved under exactly similar circumstances, 58.1 parts of gold.

These facts will render it very evident that if some means can be devised for recovering the bromine which has been used in the treatment of the ore much better results can be obtained than can be obtained by chlorination. Several plans have been devised for accomplishing this result, but only one has as yet been put into practical working in a mill. It consists in adding to the liquor which has acted upon the ore, and which stills contains a large excess of bromine as well as some bromides, sufficient chlorine or oxidizing agent and acid to liberate the bromine from the bromides and then to distil off the bromine by steam. The amount of liquid which it is necessary to distil off in order to free an aqueous solution of bromine from its bromine is surprisingly small. Using a solution of about fifteen pounds in 100 gallons the bromine is practically gone when about five per cent. of the liquid has distilled over. The liquid thus freed from bromine is in an ideal condition for the precipitation of gold, and this may be accomplished by any convenient method. It will then be seen that the process is in the main identical with chlorination as far as apparatus is concerned, except that to the liquid an addition of chemicals is made and

it is then heated up by steam and a small portion distilled off before precipitation.

The necessary steps may be stated as follows:

1. Crushing the ore preferably in a Blake crusher.
2. Drying.
3. Reducing to twenty to thirty mesh preferably by rolls.
4. Roasting, unless it is already almost completely oxidized.
5. Treating with bromine solution, preferably by agitation in a barrel, under some circumstances also by percolation in vats.
6. Drawing off the liquor and washing the ore with weak wash water from a previous operation, and after that either with water, or else with liquor from which the gold has been precipitated in a previous operation.
7. Adding to the strong liquor from leaching the ore sufficient chlorine, bleaching powder and acid, potassium permanganate and acid, or some other oxidizing agent, in sufficient quantity to liberate the bromine present as bromides.
8. Distilling off the bromine by steam.
9. Precipitating the gold.

With regard to the reduction of the ore to a proper fineness nothing need be said. It should be done exactly as if the ore were to be treated by chlorination.

The roasting, however, need not with ores which lose gold on roasting be carried so far as if the ore were to be chlorinated. The reasons why this is true are evident from a consideration of what has been said with regard to the differences in properties between chlorine and bromine; the less powerful oxidizing action of the bromine, the greater solvent power on the gold, and above all the possibility of making a strong solution of bromine, while in chlorination the solution is weak, render it possible to stop the roasting at a very much less perfect degree. The advantages of this will be apparent when the losses in gold, which occur during the last stages of roasting, are taken into account,[1] losses which result both from the volatility of the gold itself, and also from the fine particles being carried away by the current of air in the furnace. In roasting tellurides especially the losses in gold are enormous if the roasting is carried

[1] Rose, Metallurgy of Gold, p. 222.

too far. Küstel records the loss of twenty per cent. of the gold present during the oxidizing roasting of certain tellurides of gold and silver, and states that it is not a mechanical loss, but is due to volatilization. Rose records many other results which place beyond doubt the great advantage of restricting the roasting as much as possible. This loss of gold toward the end of the roasting causes one of the greatest difficulties in chlorination. Since one per cent. of sulphur requires 200 pounds of chlorine per ton of ore, the loss must be borne because it is necessary to carry on the roasting to a high degree, otherwise no gold at all, or only a part, will be obtained.

The mechanical treatment of the ore during the action of the bromine upon it is not different in any material way from the treatment with chlorine ; the ore is charged into the barrel in the same way. The bromine solution is added at the bottom, through the pipe which serves to draw it off again after the treatment. If the percolation process in vats is used the bromine solution is introduced into a covered vat, using the same precautions to avoid packing of the ore, etc., that are now used in the vat process for chlorination, and in the cyanide process.

After the ore has been acted upon by the bromine solution for a sufficient length of time the liquor is drawn off at the bottom and weak wash water from a previous operation introduced at the top of the ore, the first liquor, which is strong, being sent to a strong liquor tank, and the subsequent weaker liquor being reserved in a weaker liquor tank for subsequent use in leaching ore. From the strong liquor tank the solution runs into a still. One form of apparatus which has been used successfully, but which is now being superseded by an improved form consists of a covered stone tank heated by live steam, and provided with an outlet for the vapors, which leads to a stoneware condenser. Into the condenser, weak liquor from the weak liquor tank is allowed to enter with the vapors and in this way a bromine solution of the proper strength to run into the barrel with more ore is obtained. To the liquid in the still, before steam is turned on, bleaching powder and oil of vitrol, or

potassium permanganate and oil of vitrol, is introduced in sufficient quantity to free the bromine present as bromides. The chemicals used for this purpose in the mill have been bleaching powder and oil of vitriol. It may be asked why, if bleaching powder and acid are to be used to liberate the bromine from bromide, it would not be just as well to treat the ore with them in the first instance; to this it may be answered that in the process only as much chlorine is used as will liberate the amount of bromine which has actually combined with the ore, whereas in chlorination an excess is used which amounts to several times this amount. After the bromine is out of the liquid in the still it is run hot into the precipitating tanks, where it may be precipitated in any desired way. The only difference between the precipitation here and in chlorination is that here there is no troublesome excess of chlorine to be disposed of by sulphur dioxide or to use up large quantities of precipitants. The precipitant actually used in the mill has been powdered sulphide of iron, which in the hot liquor precipitates the gold quickly and completely. The gold is caught in a filter press and refined as usual.

Where ores are to be treated, in which the gold is present partly in too large pieces to dissolve rapidly in the bromine solution, the washed ore must be allowed to run over amalgamated plates, and as the gold is in perfect condition to amalgamate, it is easily caught.

The details of the process have been worked out by the Nellie Bly Gold Mining & Reduction Co., in Magnolia, Colorado, using an ore which has never before been successfully treated. It is a siliceous ore containing from $8.00 to $20.00 in gold per ton as tellurium compounds and nothing else of value. It cannot be amalgamated, concentrated, treated by the cyanide process, nor shipped to the smelters in Denver at a profit, and consequently presents a very difficult problem which has, however, been solved with entire success.

The process is also about to be introduced in other localities, and it seems entirely probable that it may in the near future displace chlorination to a great extent, at least.

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A SIMPLE METHOD FOR DETERMINING THE NEUTRALITY OF THE AMMONIUM CITRATE SOLUTION USED IN THE ANALYSIS OF FERTILIZERS.

BY N. W. LORD.

Received April 6, 1896.

IT is well known that the preparation of a strictly neutral solution of ammonium citrate requires considerable judgment, owing to the uncertainty of the color change when using ordinary indicators in the presence of salts of citric acid.

Even when using corallin, as directed in the official methods of the Association of Official Agricultural Chemists, some uncertainty remains. "Huston's Method" with alcoholic solutions of calcium chloride, while very exact, is a little troublesome.

The following method has been in use in my laboratory for over a year and has proved rapid and exact. I have used it only with litmus as the indicator as the tint so obtained is very easily matched, probably corallin or cochineal would do as well.

The method consists in establishing an accurately neutral color for comparison, by superimposing two tubes, one containing acid litmus, and the other alkaline litmus, and looking through both at once. Then comparing this with the diluted citrate solution, colored to the same depth with the same amount of litmus tincture. The details are as follows:

Add pure litmus solution to about 200 cc. of neutral distilled water until it is colored distinctly, but not deeply. Take half of this and dilute further with its own volume of water. Now take three clear fifty cc. "Nessler tubes," fill two of them with the diluted liquid, and the third to the same depth with the stronger solution. To one of the two first add a drop of dilute sulphuric acid, to the other a drop of ammonia. Set these tubes one in front of the other, so that the light passes through both, thus giving a strictly neutral purple color; a little care will enable one to see them almost like one tube against a sheet of white paper in a ground glass. It makes no difference which tube is in front. Now to the liquid in the third tube containing the stronger solution (which is obviously equal in color depth to the double thickness of the first two tubes), add five cc. of the citrate solution to be tested, and compare the color

produced with the color shown by the doubled tubes. The slightest acidity or alkalinity of the citrate is at once shown by difference of tint; the test is very sensitive. The amount of acid or alkali needed to bring it right, can then be easily obtained by adding one-half normal sulphuric acid or ammonia; then by calculating to the five cc. taken, the necessary addition to the "stock" solution can be found and when made the solution re-tested with remainder of the colored water. The operation is very rapidly performed and the results surprisingly exact. Solutions so neutralized, when tested by Huston's method, have always been found exactly correct. The litmus solution should be prepared from the alcohol extracted litmus, as directed by Sutton.

THE COPPER ASSAY BY THE IODIDE METHOD.

By Albert H. Low.

Received March 23, 1896.

The last edition of Dr. Peters' Modern Copper Smelting contains a description of the writer's modification of the copper assay by the iodide method. The following description of the same method embodies whatever changes have been deemed desirable up to date as the result of almost daily work upon copper ores and products. For the most accurate technical work I prefer it to all other methods. For practical work it exceeds the electrolytic method in accuracy, notwithstandiug that the latter, when every precaution is taken, is perhaps theoretically more accurate.

COPPER ASSAY BY THE IODIDE METHOD.

Prepare a solution of sodium hyposulphite containing about nineteen grams of the pure crystals to the liter. Standardize as follows: Weigh accurately about 0.200 gram of pure copper foil and place in a flask of about 250 cc. capacity. Add five cc. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water, and thoroughly boil off the red fumes,—a very essential point. Now remove from the lamp and add six to seven grams of crystallized zinc acetate, roughly weighed, and about fifteen cc. of water. Instead of adding the of zinc acetate in this way, a cold saturated solution may be kept on hand and about twenty

cc. taken, the additional fifteen cc. of water being then unnecessary. Heat to boiling for a moment and then cool to ordinary temperature, and dilute to a bulk of about fifty cc. Now add about three grams of potassium iodide and shake it about gently until dissolved. Cuprous iodide will be precipitated and iodine liberated according to the following reaction: $2(Cu.2C_2H_3O_2)+4KI=Cu_2I_2+4(K.C_2H_3O_2)+2I$. The free iodine colors the mixture brown. Titrate at once with the hyposulphite solution until the brown tinge has become weak and then add sufficient starch liquor to produce a marked blue coloration. Now continue the titration cautiously until the blue tinge has entirely vanished. When almost at the end allow a little time after the addition of each drop to avoid passing the point. One cc. of the hyposulphite solution will be found to correspond to about 0.005 gram of copper. In the assaying of ores, etc., when half a gram is taken, one cc. of the standard hyposulphite would then equal about one per cent. copper. The reaction between the hyposulphite and the iodine is: $2(Na_2S_2O_3)+2I=2NaI+Na_2S_4O_6$. Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about half a gram of starch with a little water and diluting with hot water to about 250 cc. It should be used cold and must be prepared frequently for regular work, as it does not keep very well. The hyposulphite solution made of the pure crystals and distilled water appears to be very stable, showing no appreciable variation at the end of a month, when kept under reasonable conditions.

TREATMENT OF ORES.

Treat half a gram of the ore in a flask of 250 cc. capacity with five or six cc. of strong nitric acid and boil gently nearly to dryness. Then add five cc. of strong hydrochloric acid and again boil. As soon as the incrusted matter has dissolved add five cc. of strong sulphuric acid and heat strongly, best by manipulating the flask in a holder over a small naked flame, until the more volatile acids are expelled and the fumes of the sulphuric acid are coming off freely. Allow to cool and then add twenty cc. of cold water and heat the mixture to boiling to thoroughly dissolve any anhydrous sulphates of iron, etc. Now

filter to remove more especially any lead sulphate and receive the filtrate in a beaker about two and one-half inches in diameter. Wash the flask and filter with hot water and endeavor to keep the volume of the filtrate down to about fifty or sixty cc. Place in the beaker two pieces of sheet aluminum, which, for the sake of convenience in subsequent washing, may be prepared as follows: Stout sheet aluminum, say about one-sixteenth of an inch in thickness, is cut into pieces an inch and a half square, and then the four corners are bent, for about a quarter of an inch, alternately up and down at right angles. This scheme prevents the pieces from lying flat against each other or upon the bottom of the beaker, and their washing is thus facilitated. The same pieces of aluminum may be used repeatedly, as they are but little attacked each time. Add five cc. of strong sulphuric acid, cover the beaker and heat to boiling. Boil strongly for about seven minutes. Unless the bulk of the solution is excessive this will be quite sufficient with all percentages of copper. Ordinarily the aluminum will be found to be clean and nearly or quite free from precipitated copper. If, by chance, the copper adheres to any considerable extent, it will usually become loosened by a little additional boiling, or it may be removed by the aid of a glass rod. Transfer the solution back to the original flask, and, by means of a wash bottle of hot water, rinse in also as much of the copper as possible, leaving the aluminum behind. Drain the beaker as completely as possible and temporarily set it aside with the aluminum which may still retain a little copper. Allow the copper in the flask to settle and then decant the liquid through a filter. Again wash the copper similarly two or three times with a little hot water, retaining it as completely as possible in the flask. Finally wash the filter once or twice and endeavor to rinse all metallic particles down into the point. Now pour upon the aluminum in the beaker five cc. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water and warm the beaker gently, but do not heat to boiling, as the aluminum would be thereby unnecessarily attacked. See that any copper present is dissolved and pour the warm solution through the filter last used, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main

portion of the copper. At this stage do not wash either the aluminum or the filter, but simply remove the flask and set the beaker in its place. Heat the mixture in the flask to boiling and see that all the copper is dissolved. Then add about half a gram of potassium chlorate and again boil for a moment. This is to oxidize any arsenic present to arsenic acid and is a very important point. Remove the flask from the lamp and again place it under the funnel and wash the beaker, aluminum and filter with as little hot water as possible. Again boil sufficiently to remove every trace of red fumes. All the copper is now in the flask as nitrate. Add the zinc acetate and proceed from this point precisely as described with the original nitrate of copper solution in the standardization of the hyposulphite, finally calculating the percentage of copper present from the amount of standard hyposulphite required. One point, however, remains to be further explained. According to the equation previously given, half a gram of pure copper requires 2.62 grams of potassium iodide. While direct experiment shows this to be apparently true, yet it is found that with small percentages of copper, the reaction, when only the theoretical amount of potassium iodide is taken, is slow and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is therefore best to use not less than three grams of potassium iodide in any case. An excess does no harm. Silver does not interfere with the method. Lead and bismuth are without effect, except that by forming yellowish iodides they may mask the end-point before adding starch. Lead is practically removed as sulphate at a previous stage. If bismuch is suspected in any appreciable amount, simply add the starch earlier in the titration. Arsenic when oxidized as described has no influence. The return of the blue tinge in the liquid by long standing after titration is of no significance, but a quick return of the color, which an additional drop or two of the hyposulphite does not permanently destroy, may indicate either an incomplete combination of all the nitric acid with zinc, or a failure to completely boil off the red fumes when dissolving the copper in nitric acid. The assay in such a case is spoiled. This trouble may be avoided by carefully following the directions

given and not guessing at strengths or quantities. The amount of zinc acetate recommended is a safe excess. Sodium acetate does not appear to work as satisfactorily.

For the assay of alloys, etc., the necessary modifications of the foregoing scheme are obvious.

The foregoing scheme directs the use of five cc. of dilute nitric acid for dissolving the copper previous to titration and prescribes six to seven grams, or about twenty cc. of a saturated solution of zinc acetate as a safe excess of neutralizing agent. It is obvious that if most of the nitric acid be boiled away the amount of zinc salt necessary is greatly reduced. In such a case, however, it is perhaps best, for safety's sake, not to use less than one-half the prescribed quantity. Half the zinc salt may thus be saved at the expense of a little more time. This is the ordinary practice in my own laboratory.

DENVER, COLORADO.

ON TWO SOURCES OF ERROR IN SUGAR HOUSE ANALYSES.

BY EDMUND C. SHOREY.

Received March 10, 1896.

INCIDENTAL to the study of the action of water of different temperatures on bagasse, I have had occasion to make some determinations which throw some light on a source of error in fiber determinations.

Finely cut cane was washed with cold water until the polariscope reading in a twenty cm. tube was 0; the excess of water squeezed out in a press, and three portions of fifty grams each taken. In one the moisture was determined by drying to constant weight in an air bath at 105° C.; the two others were treated with boiling water; one for five minutes and the other for two hours. The quantity of water used was in each case just sufficient to cover the cane chips, and at the expiration of the time the water and the chips were poured on a filter and washed four times with cold water, using each time the same quantity of wash water as was used in the original treatment. The filtrate so obtained was evaporated to dryness over a waterbath, dried at 105° C., and calculated to percentage of dry sub-

stance left after the exhaustion of sucrose with cold water. The filtrates obtained were decidedly milky, and this no amount of filtering would remove. A portion of filtrate on standing undisturbed for six days had *not* become less milky, and had thrown down *no* deposit.

The cane was prepared by cutting to fineness of saw dust in a meat chopper, and determinations have in all cases been made in duplicate.

The mean of six fairly mean concordant determinations is as follows:

(1) Treatment for five minutes with boiling water extracted seven and two-tenths per cent. of dry substance.

(2). Treatment for two hours with boiling water extracted twelve per cent. of dry substance.

To show the amount of error likely to result from using varying quantities of water and varying the time of boiling; suppose that the fiber and dry substance from the treatment with cold water was ten per cent. of cane, we would have:

	Per cent.
Fiber extraction with cold water	10.0
" " " hot water five hours	9.3
" " " " " two hours	8.8

Dr. Beeson, of Audubon Park Sugar School, has pointed out in this Journal the errors in fiber determinations likely to result from the varying amounts of fiber in different parts of the same stalk of cane. This can be overcome, I think, by taking a sufficiently large sample and reducing it to a very fine state of division; but if fiber determinations by different chemists are to be comparable, some uniform method must be agreed upon. This method should provide for the fineness of division of cane or bagasse, the quantity of sample to be taken, the quantity of water to be used, the number of times washing, and the length of time of boiling.

In calculating the extraction by formulas similar to those given by M. Trubek in this Journal (Dec., 1895), I prefer to dry the residue from alcoholic extraction and call this fiber. The object being simply to compare the fiber in the cane with that in the

bagasse, and this method I find gives more uniform results with a minimum of labor.

A second source of error in sugar house analyses to which I wish to draw attention is in the determination of albuminoid nitrogen as commonly carried out.

In the official method for albuminoid nitrogen in finding stuffs the directions are to heat to boiling, add cupric hydrate, filter when cold and wash with cold water. In the determinations of albuminoid nitrogen in cane juice made by W. Maxwell, and published by him in a Bulletin of Louisiana Experiment Station, this method was modified, but for what reason I am unable to say. According to this modified method the juice was heated to boiling, cupric hydroxide added, boiled ten minutes, filtered hot and washed with hot water. Both these methods introduce a serious error, owing to the fact that when cane juice in its natural acid condition is heated a change is brought about in the aluminoid nitrogen contained therein, and in consequence the amount of aluminoids as determined by either of these methods is not really that which is in the juice in the plant, but that which is left from the action of heat and the acid in the juice.

During the past two years I have made a large number of determinations, as follows: I. Total nitrogen in juice; II. Albuminoid nitrogen in cold juice; III. Albuminoid nitrogen in juice which had been heated to 71°–72° C.; IV. Albuminoid nitrogen in juice which had been boiled one minute. For total nitrogen the Gunning method was used, and for albuminods cupric hydroxide was added to cold juice, filtered cold and washed with cold water, the precipitate and filter paper treated by Gunning method. In each case twenty cc. of juice have been used, and the results calculated to percentage of total solids as given by Brix spindle; the difference between total nitrogen and albuminoids has been called amides and calculated to asparagins.

As the results have been the same in all cases, I give below two analyses which I have already communicated to the Planter's Monthly, (Honolulu).

1. Brix, 17.3; Purity, 91.

Acidity, 100 cc. juice = ten cc. $\frac{N}{10}$ alkali.

Total nitrogen 1.115 per cent. of total solids.

	Per cent. of nitrogen compounds. Albuminoids.	Amines.
Cold juice	95.5	4.5
Juice heated 71°–72° C.	87.5	12.5
Juice boiled one minute	86.7	13.3

2. Brix, 18.2; Purity, 90.9.

Acidity, 100 cc. juice = 11.3 cc. $\frac{N}{10}$ alkali.

Total nitrogen 1.032 per cent. of total solids.

	Per cent. of nitrogen compounds. Albuminoids.	Amines.
Cold juice	93.5	6.5
Juice heated 71°–72° C.	81.4	18.6
Juice boiled one minute	77.4	22.6

Although I have in these analyses designated the body or bodies formed from the albuminoids by heat amines, I am of the opinion for several reasons that they are peptones or soluble albuminoids. I am at present investigating the matter. Whatever they are, the fact remains that the albuminoid nitrogen determinations on cane juice as carried out by any method which calls for the heating of the raw acid juice are not reliable.

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KOHALA, HAWAII.

REVIEW.

BERTHELOT'S CONTRIBUTIONS TO THE HISTORY OF CHEMISTRY.[1]

Marcellin Berthelot, Professor of Chemistry in the Collège de France, Perpetual Secretary of the Academy of Sciences, Senator, Minister of Public Instruction, and recently appointed Minister of Foreign Affairs, known to the scientific world by his masterly researches in synthetical chemistry, has added to these honors that of editing the most important and far-reaching documents pertaining to the history of chemistry ever brought to light.

The six handsome quarto volumes published by him between the years 1887 and 1893, contain the most ancient Greek, Arabic, Syriac, and Latin treatises on alchemy and technical chemistry preserved in the great libraries of the Old World. Besides reproducing the original text of these precious manuscripts, these volumes contain complete translations of many treatises, analyses of the contents of others, and critical studies of their mutual relations, their sources and authorship, as well as erudite essays on the chemical knowledge exhibited in them. The six volumes form two distinct works: three of the volumes bear the title: "Collection des anciens Alchimistes Grecs," and three of them, "La chimie au moyen âge," each volume having, moreover, specific sub-titles more exactly indicating its contents.

Not having seen any adequate review of these works in English, I propose in this article to examine their scope, contents, and manner of treatment, as well as to show some of the more important changes resulting from Berthelot's historical studies. The existence of ancient Greek and Arabian manuscripts had long been known; Reuvens, and later Leemans, of Holland, had published summaries of certain papyri preserved in Leyden, more than forty years before, but in such a fragmentary manner as merely to excite curiosity. Ferdinand Hoefer, the French historian of chemistry, and Herman Kopp, the erudite German, had made partial use of some of the manuscripts, but it remained for Berthelot to collect and compare the diverse copies, to reproduce and translate them for the benefit of students. This he could scarcely have accomplished without the aid of the French Government, both series being "published under the auspices of the Minister of Public Instruction." Government cooperation was brought about through a report made by Berthelot to

[1] Read before the Washington Section of the American Chemical Society, March 12, 1896.

the "comité des travaux historiques et scientifiques," and adopted by them in 1884. This report directed attention to the existence of Greek alchemical manuscripts and to the utility of their publication, owing to the great light they throw on the history of natural science, the technology of metals and ceramics, and the history of philosophy in the first centuries of the Christian era.

The difficulties of deciphering, transcribing, and editing Greek, Arabic, Syriac and Latin manuscripts were prodigious, and Berthelot was fortunate in securing scholars of eminence to assist in the task. In dealing with the Greek papyri, he was aided by Ch. Em. Ruelle, of the Bibliothèque Sainte Geneviève, Paris, and by André Berthelot, son of the editor; the Arabic scholar, Professor Houdas, and the Syriac linguist, Rubens Duval, also contributed their learning, each in his own sphere.

The "Collection des Alchimistes Grecs," opens with an "Introduction" by Berthelot, which occupies 268 pages; this forms an important contribution to the history of chemistry, based upon a critical study of the ancient treatises; he agrees with other historians in tracing the birth of alchemical ideas to Egyptians, whence they reached Europe through Greeks.

Certain Greco-Egyptian papyri, preserved in Leyden, are of the greatest interest; several of them treat of magical formulas, incantations, love philtres, dreams, and similar gnostic notions; one of them, known as "Papyrus X," is a treasury of information on metallurgical operations, at so early a period as the third century of the Christian era. It was found in a tomb at Thebes, secured by the Swedish Consul at Alexandria, Anastasi, and presented by him to the Netherlands in 1828. Berthelot conjectures it is one of the ancient Egyptian books on the preparation of gold and silver, which escaped the destruction ordered by Diocletian in 290; an order issued lest the people using them should grow rich by their art and revolt against the Romans.

This precious document contains one hundred and one chemical and alchemical recipes, followed by ten paragraphs taken from Dioscorides. The recipes are for making alloys to be used in the manufacture of cups, vases, images, and other objects of the goldsmith's art, also processes for soldering metals and superficially coloring them, besides formulas for making gold and silver inks. The text is full of grammatical errors and ignorant spellings, which show the writing to have been the work of an uneducated artisan; the recipes are not arranged in order, several appear in duplicate; they exhibit no indication of chicanery, although some of the methods are unprofitable. The

whole papyrus, in short, is evidently the memorandum-book of a goldsmith (or silversmith), engaged in attempts to imitate gold and silver for fraudulent purposes. Only one author is cited, "Phimenas," who is probably Pammenes, author of recipes occuring also in other manuscripts. The preparation of *asem*, an amalgam of copper and tin, plays a prominent part among the recipes for imitating gold. But time forbids a full analysis of this remarkable manuscript; as a result of Berthelot's careful study of this and analogous treatises, he comes to the conclusion that the doctrines of alchemy concerning the transmutation of metals did not originate in the philosophical views of the constitution of matter, as generally supposed, but in the practical experiments of goldsmiths occupied in making fraudulent substitutes for the precious metals. The "Introduction" contains a chapter on the relations between the metals and the planets, of Chaldean origin, and constant occurrence in the early writings, which is illustrated by facsimiles of several manuscript pages. Another chapter is devoted to the figures of apparatus occurring in the treatises of the eleventh to fourteenth centuries; these include water-baths, digestors, aludels, alembics and a great variety of apparatus for distillation.

The sixth chapter of the introduction is divided into twelve sections; these deal with several Greek manuscripts, notably those preserved in the libraries of St. Mark, Venice, the Escurial, the Vatican, Rome, Gotha, and in Munich, appertaining to the eleventh to fourteenth centuries; of these we note only a few features. At the beginning of the MS. of St. Mark is one of the earliest of chemical bibliographies; it gives the title of fifty-two treatises, verily not in modern style, yet quite suggestive; among them are the following: "Emperor Heraclius, eleven chapters on the manufacture of gold." "Justinian, five chapters on the secret art." "Heliodorus, on the divine art." "Theophrastus, verses on this art." "Moses, on the diplosis (doubling) of gold." "Lexicon of the gold maker, in alphabetical order."

This association of names of Emperors of Rome, Greek classical writers and the Hebrew law giver with chemical and alchemical treatises is characteristic of the period at which they were compiled and by no means denotes actual authorship; the names of prominent men were given to the treatises in order to add to the dignity and authority of the writings. This custom prevailed as late as the sixteenth century, and in certain cases to be noted hereafter, gave rise to undeserved honors. An entire group of writings have been ascribed to Democritus, giving rise in Egypt to what may be styled the school of Democritus. A certain Zosimus of Panoplis is credited with a veritable ency-

clopedia of the sacred art, a work which occupies ninety pages of Berthelot's volume.

The Collection des Alchimistes Grecs comprises no less than 160 different treatises on the science of Hermes. Many of these are fragmentary in the extreme, extending to only six lines, and even less. All are composed in an archaic, enigmatical style, combining in one undecipherable medley, chemical terms of obscure meaning, magical formulas, astrological notions, citations from mythical authors, and mystical allusions to a philosophy long since buried too deep for present resurrection. It is not surprising that commentators early felt the need of lexicons of the sacred art, and such are preserved in these volumes; unfortunately, however, the definitions are no clearer than the words defined; one word was often used for a score of different objects and processes, and a single article was known by a dozen different names. To convey to readers any idea of these extraordinary literary productions by citations, is hardly practicable in the space available, for passages lose much when removed from their original settings. The actual chemical knowledge exhibited in these ancient manuscripts is varied, and yet indefinite, owing to the numerous obscure expressions; the authors were acquainted with a large number of ores, minerals, earthy substances, and saline bodies, as well as vegetable and animal products, but their ignorance of the mineral acids and their important derivatives, limited them to products obtained by aqueous solution, distillation and the action of heat. Of scientifically classified knowledge there is no trace; the alleged opinions of mythical writers are given as authoritative, and information is imparted in the tedious form of dialogues between philosophers, who remind one of the Scotchman's definition of metaphysicians: "Poor bodies discussing things of which they know nothing, in a language neither of them can understand." Many of the writings contain reverent acknowledgements of the Deity and other evidences of piety. There is a good deal of duplication, arising from the introduction into an essay of passages from another, generally without acknowledgement.

Berthelot remarks incidentally that the term *Philosophers' Stone* does not occur in writings earlier than the seventh century, although the central idea is much more ancient.

Each of the three quarto volumes which constitute Berthelot's "La chimie au moyen âge" bears an independent title; that of the first volume reads: "Essay on the transmission of the knowledge of Antiquity to the Middle Ages; transmission of technology; translations of Arabico-Latin treatises, with a new

version of the *Liber Ignium* of Marcus Graecus, and an original edition of the *Liber Sacerdotum*."

This volume covers the period from the fall of the Roman Empire to the thirteenth century, thus filling the gap between the ancient Greek alchemists and the Latin writers of the later epoch, a period which had been previously unworked or misunderstood. Berthelot finds that the transmission from the earlier to the later era was accomplished by two agencies; first through the Arabians, who succeeded to the literary and scientific wealth of the Greeks. The Arabic treatises, preserved in the Mohammedan libraries of Spain, were translated into Latin and thus became for Western nations the sources of their knowledge in medicine, alchemy, mathematics and philosophy. Some of these translations were collected and printed in the seventeenth century in the works entitled *Theatrum chemicum*, (5 vols., 1613–22), and *Bibliotheca chemica*, of Mangetus, (2 vols., folio, 1702), and Berthelot discovered in these Arabico-Latin treatises entire passages from the ancient Greek Alchemists.

The connection between the Greeks and Arabians was not however immediate, but through the Syrians, who were among the first to translate the philosophy and science of the Greeks into an oriental tongue. These Syraic versions form the subject of the second volume.

A second link between the Greeks and the Latin alchemy was more directly forged, though difficult of recognition; the processes used in industrial arts and metallurgical operations by the Greeks had been adopted by the Latins as early as the time of the Roman Empire, and this chemical technology was preserved through centuries of intellectual degradation to the beginning of the Middle Ages.

The most ancient Latin treatises on chemical technology are the *Compositiones ad tingenda*, dating from the close of the eighth century, and the *Mappæ clavicula*, written before the tenth century. These are collections of recipes for industrial processes analogous to those in the Leyden papyrus, and forming links in a chain that extends from that ancient work through the treatises of the Middle Ages to the modern "Workshop Recipes" and "Manuels Rorets." The full title of the *Compositiones ad tingenda* is as follows: [Translation.] "Recipes for coloring mosaics, skins and other objects, for gilding iron, for using minerals, for writing in letters of gold, for soldering metals, and other technical documents." The following are some of the subjects treated: The coloring of artificial stones, used in the manufacture of mosaics; the manufacture of stained glass; the dying of skins in purple, green, yellow and reds; the dyeing of

wood, bone and horn; a list of ores, metals, earths and metallic oxides used in jewelry and in painting; a number of recipes for gilding on glass, wood, skins, garments, and the metals. All these topics are treated in barbarous Latin, bordering on a species of jargon; some were originally written in Greek and copied by ignorant scribes in Latin letters, which shows the influence of Constantinople. In one of the sections on ores, the word "vitriol" occurs for the first time, being the eighth century, and in the correct significance of an impure ferrous sulphate. A very rational grouping of substances occurs in this work, the minerals and earths are by themselves, then follow gums, rosins and other products of plants, and thirdly substances derived from the ocean, such as salt, coral and mollusks yielding purple dye. A certain recipe for writing in letters of gold is practically identical with one in the Papyrus of Leyden.

A formula for making bronze shows the origin of this name, *De compositio brandisii*, Brindes being a synonym of Brundusium, (Brindisi), a town noted in Pliny's day for its metallic mirrors.

A large part of *Compositiones ad tingenda* is reproduced in the work entitled *Mappæ clavicula*, of which the earliest known manuscript dates from the tenth century. This latter treatise contains recipes for making gold, for multiplying gold and imitating the precious metal, closely resembling those of the ancient Greek papyri. In this connection cautions are given to conceal the secrets, and an incantation is prescribed to be used during the operation. Exceeding interest attaches to the fact that the use of the hydrostatic balance in analysis of an alloy is clearly described, for this proves that the knowledge of this instrument did not pass through Arabian channels, and possibly came down direct from Archimedes.

The *Liber ignium ad comburendos hostes*, by Marcus Graecus, is one of the most ancient Latin treatises on Greek fire, dating from the twelfth or thirteenth century, and is probably a translation from an earlier Greek work transmitted through Arabian channels. It deals with instructions for making Greek fire, so called, phosphorescent materials, fire-proofing substances, and the preparation of fuses and petards, composed in part of saltpeter. Greek fire itself, however, dates from the second century, B. C., and phosphorescent stones are named in the much earlier Greek alchemical manuscripts.

Berthelot devotes an interesting chapter to the discovery of alcohol. This product of distillation first appears under the name *aqua ardens*, and the term alcohol in its present signification does not occur before the middle of the fourteenth century; the

term *spiritus vini* is also comparatively modern, and *aqua vitae* seems to have been applied to alcohol for the first time by Arnald de Villanova, who died in 1314. The fact that wine yielded an inflammable substance, was, however, already noted by Aristotle, but this body was not isolated. Rhases has been given credit for acquaintance with alcohol, but this is erroneous.

The preparation of alcohol by distilling wine is, however, mentioned in a copy of the *Mappæ clavicula*, written in the twelfth century, and in the *Liber ignium* of Marcus Graecus.

In attempting to trace to their origin, Latin treatises which claim to be translated from Arabic, Berthelot made the important discovery that they are fraudulent, the Arabic manuscripts having no existence. Thus the chemical works attributed to the Arabian physician Jâbir ibn Hayyan (Abu Musâ), commonly called Geber, are shown to be fictitious, and the great reverence paid to him as a pioneer in chemistry has been misplaced. The whole history of chemistry has been falsified by giving credit to the Arabians for knowledge which really belonged to a period five hundred years later.

Yet the historical personage Geber, who lived in the ninth century, left many treatises in Arabic, now preserved in Paris and Leyden, and the translation of these occupy 100 pages of the third volume; they are very different from the works so widely known as Geber's, which are found in Latin, French, German, and English.

In like manner the current alchemical treatises ascribed to Raymond Lully are shown to be fictitious, yet his works on philosophy in the Provençal language are extant.

The Pseudo-Arabic works in their Latin form contain, however, traces of the ancient Greek alchemical writings, and to endow them with authority the writers referred the text to mythical personages; and as these were cited by later authors who did not doubt their genuineness, the pseudo-treatises acquired undeserved renown. Students of alchemy who have been revelling in the works of Morien, Kalid, Zadith, Mary, and the collection of citations entitled *Turba philosophorum*, are loth to have their antique idols shattered, but this is the fate of every branch of human knowledge when subjected to the modern methods of searching analysis.

The second volume of "La chimie au moyen âge" has the subtitle: Syriac Alchemy, comprising an introduction, and several treatises of Syriac and Arabic alchemy from the manuscripts in the British Museum and Cambridge; text and translation."

The existence of Syriac alchemical manuscripts in the British

Museum was pointed out to Berthelot by Prof. Richard Gottheil, of Columbia University, New York City. The most important of these, entitled "The Doctrine of Democritus," was translated from Greek between the seventh and ninth centuries. It begins with a charge of self-purification, followed by a key to the symbols used in the manuscript; these signs resemble in part those occurring in the writings of the earlier Greek alchemists. The first section of the "Doctrine" is called "The Preparation of Gold," the second is called "On the Philosophers' Stone," and the succeeding parts contain a collection of recipes, processes with metals, as well as with sulfur, antimony, arsenic, and ores, analogous to the Leyden papyrus and the *Mappæ clavicula*. Rude drawings of apparatus accompany the text. The writer shows acquaintance with a very large number of chemical substances.

The Library of the University of Cambridge possesses a Syriac manuscript, which is a translation of portions of the Greek writings of Zosimus, Democritus, and others. It is similar in character to the preceding.

Volume III of "La chimie au moyen âge" has the sub-title: "Arabian Alchemy, comprising an historical introduction, the treatises of Crates, el-Habîb, Ostanes and Djâber from manuscripts in Paris and Leyden; text and translation."

The Arabic treatises here named are the genuine writings, not the fictitious ones known only in Latin. The first Mohammedan writer on alchemy was Khâled ben Yezid ibn Moaouīa, Prince Omeyyade, who died in 708; he is a historic personage and the reputed teacher of Djâber. Only the titles of his works have come down to us. Djâber, the Geber of the Latins, was, however, the great master of the art and enjoyed the highest reputation throughout the Middle Ages; he is credited with 500 treatises, an Oriental exaggeration. Six of these are here collected and translated. They exhibit evidence of Moslem faith on the part of the author; he shows familiarity with the hydrostatic balance, with many species of minerals (of which an ingenious classification is given), and he discourses on the changes in volume produced by heat and by cold; at the same time he admits using allegorical and obscure language in all his works. There is no reference to the mineral acids, to nitrate of silver and other chemicals that Geber is supposed to have known. Perhaps the most clever passage in his works is the following from the "Book of Mercy:"—

"I saw that persons engaged in attempts to manufacture gold and silver were working ignorantly and by wrong methods; I

then perceived that they were divided into two categories, the dupers and the duped. I had pity for both of them."

Berthelot's superb volumes comprise more than 2600 pages, and much of the contents defies review. Besides these original documents he has published two works dealing in more popular style with the periods of alchemy and Middle Age chemistry. These are entitled: "Les Origines de l'Alchimie," (1885), and "Introduction à l'Étude de la Chimie des Anciens et du Moyen Age" (1889); the latter is largely reprinted in the quarto volumes; all are charmingly written, well illustrated, and well indexed.

Berthelot had extraordinary qualifications for the task and enjoyed unrivalled opportunities, and the result is a magnificent contribution to the history of chemistry, of utmost interest to the chemical student as well as to the philosopher.

H. CARRINGTON BOLTON.

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VOL. XVIII. [JUNE, 1896.] No. 6.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 20.]

THE EFFECT OF ACIDITY ON THE DEVELOPMENT OF THE NITRIFYING ORGANISMS.[1]

BY E. E. EWELL AND H. W. WILEY.

Received April 16, 1896.

FOR nearly two decades, both lay and scientific minds have been constantly perturbed by frequent announcements of the discovery of some new microbe that is seeking the destruction of ourselves or of our domestic animals. We have been warned to be on the alert for these deadly foes in the food that we eat, in the water that we drink, and in the air that we breathe. This general alarm has caused us to overlook many of the other important discoveries in the world of microscopic organisms. Indeed, the rapid development of our knowledge of the disease-producing organisms has been accompanied by an equally important advance in our knowledge of that multitude of microbes that are not only our friends, but are necessary to our existence. It is to one group of these more friendly organisms that we wish to ask attention. Passing over a host of species that are of importance in various agricultural industries, including those organisms that enable the farmer to draw upon the uncombined nitrogen of the atmosphere for an increase of his available nitrogenous plant food, we desire to consider the group of organisms engaged in the final stages of the process of transforming the nitrogen of dead animal and

1 Read before the Washington Section of the American Chemical Society, April 9, 1896.

vegetable matter into an inorganic form suitable for the nourishment of the higher forms of plant life. It will be remembered that before the nitrogen of the fallen leaf or of a scrap of meat can be readily assimilated by the higher plants, it must undergo three stages of preparation by as many sets of organisms: first, the process of "ammonization," in which nitrogenous organic matter is decomposed, yielding as final products water, carbon dioxide and ammonia; second, the process of "nitrozation," in which the nitrous ferments oxidize the ammonia to nitrous acid; third, the process of "nitration," in which the nitric ferments oxidize the nitrous to nitric acid. The organisms of the first class, the ordinary putrefactive ferments, have been known since the work of Schwann and Schultze, reported in 1839, and have been made familiar acquaintances by the more recent work of Pasteur and others. More than thirty species of bacteria and twenty species of molds and yeasts were isolated from the soil and studied in regard to their ammonizing power in 1893 by Èmile Marchale, a Belgian investigator, the detailed results of whose experiments one of us (Ewell) has had the pleasure of placing before American readers in the form of a translation published in *Agricultural Science* about a year ago. Although our knowledge of this class of organisms has been greatly enlarged, their study from the standpoint of the practical agriculturist is still a very promising field of investigation.

The two remaining stages of the process, in which the ammonia formed by the putrefactive ferments is changed to nitric acid, constitute the process of nitrification, a term that is often used to include all three of the above transformations. Until very recently this was generally supposed to be a purely chemical phenomenon and quite independent of the action of living organisms. Pasteur, reasoning from analogy, had expressed the opinion that the process was dependent upon the activity of a living ferment, but it was not until the investigations of Schloesing and Müntz in 1877 that the dependence of the phenomenon upon living organisms was given experimental proof. Warington, in England, at once repeated these experiments and obtained results that left no doubt as to the nature of the process.

The existence of a nitrifying ferment having thus been demonstrated, the contest that at once began for the honor of its isolation was such a one as has rarely been seen in the scientific world. Warington and the Franklands, in England; Heraeus, Frank, Hueppe, Celli and Zucco, on the continent of Europe; Jordan and Richards, in America; all of these were prominent in this strife. As late as 1887, Frank asserted that the failure of the numerous attempts to isolate the ferment should be interpreted as evidence of its non-existence. For thirteen years the contest continued. The efforts of Warington, of the Franklands, and of Jordan and Richards, were just beginning to lead to tangible results, when, in 1890, a new worker appeared on the field in the person of Winogradsky, a Russian, working at Zurich. While many facts had been learned and many important observations had been made by the previous investigators, it was left for the worker last named to effect the first thoroughly satisfactory isolations of the nitrifying bacteria and to study them in pure cultures. These results were made possible by his finding a solid culture medium upon which these organisms grow well. Hosts of species had been isolated from the soil, from the air, and from natural waters by growth upon various solid media made by use of gelatine or agar-agar, but none of them possessed nitrifying power. Hence it had been concluded that the nitrifying ferment was unable to grow in these media, which were abandoned for the tedious dilution method. Winogradsky's medium was composed of gelatinous silica and nutrient salts. While its preparation is somewhat difficult and it apparently offers a pabulum for the development of a much greater number of microbian species than was at first supposed, nevertheless, it is the only medium available for the satisfactory isolation of the nitrous organisms. It is possible that this medium is also necessary for the isolation of some species of the nitric organism, but Burri and Stutzer[1] have recently studied a nitric ferment that thrives on ordinary peptone-gelatine. It is quite possible that these are the first workers that have ever given an organism growing upon peptone-gelatine an opportunity to grow in an inorganic solution containing nitrites; *i. e.*, in such con-

[1] Centralblatt f. Bakterologie u. Parasitenkunde, 1895, 1, 721-740.

ditions as would determine its ability to change nitrites into nitrates. As the demonstration of the inability of the nitrous ferment to grow upon ordinary peptone-gelatine preceded the discovery that nitrification is accomplished in two stages and by the action of two distinct ferments, it seems to have been taken for granted that the nitric organism is also incapable of growing upon the organic jelly.

We have treated the history of this subject somewhat at length, yet very briefly considering the extent of its literature. This has been done in order that what is to follow may be better understood. In the light of the researches and discoveries just outlined, the farmer must regard his fields as immense bacterial cultures. He must study their needs as well as the needs of the cultures of the higher plants whose conditions of growth he has been studying so long. In order that he may expect prompt, certain and remunerative results from the use of fertilizers containing organic nitrogen, he must make sure that his soil contains ammonizing and nitrifying organisms of the highest grade of activity, and must establish the closest possible approximation to those conditions that enable these organisms to render the greatest service in their respective roles: the conditions must be such that the process of ammonization proceeds with the smallest possible loss of nitrogen from the volatilization of the ammonia formed, or from the formation of uncombined nitrogen instead of ammonia; on the other hand, the conditions should be as unfavorable as possible for the activity of the organisms of denitrification, which reduce nitrates with the liberation of uncombined nitrogen.

Bacteria are very sensitive to the conditions under which they are grown; not only do changes in these conditions alter the rate and nature of their growth, but they also change the quantity and quality of the products formed during this growth. The principal conditions that have been found to greatly influence the growth of bacteria, are amount and quality of food, supply of moisture, the proportion of oxygen in the surrounding atmosphere, temperature, the degree of acidity or alkalinity of the medium in which they are grown, the presence of substances having a retarding or accelerating action upon their growth,

and the presence of rival or helpful species. Outside of the regions where irrigation is practiced, degrees of moisture and temperature are necessarily dependent upon meteorological conditions. In the case of the nitrifying ferments, increase of the aëration of the soil by thorough stirring has been shown to be very favorable to their highest activity. The most favorable quantity and quality of the various nutritive substances and of the other materials forming the soil, as well as the influence of the presence of other bacterial species, are still questions needing further investigation.

The proportion of alkali or acid in excess in the soil and in other media for the growth of bacteria has been shown to be a matter of the first importance. It is so constant a factor that it deserves consideration separately from the class in which it would logically fall, that of the substances having a retarding or accelerating action upon bacterial growth. The influence of the reaction of the medium upon the growth of bacteria has been very prettily demonstrated by various persons engaged in the quantitative determination of the bacteria in water. At the convention of bacteriologists, held in New York in June, 1895, George W. Fuller, of the Lawrence Experiment Station of the Massachusetts State Board of Health, presented a very interesting series of results upon this subject. We have taken the liberty to use an abridgement of one of Mr. Fuller's tables to illustrate the importance of this question.

Reaction. Cc. of normal alkali required to render one liter of the medium neutral to phenolphthalein.	Relative number of colonies per cc ot water appearing upon plate cultures. Sewage.	Merrimac River water.	Lawrence City filtered water.
40	6	1	2
35	16	3	3
30	45	4	8
25	64	55	46
20	100	100	100
15	106	89	92
10	101	54	60
5	98	46	43
0	86	38	35
−5	87	26	31
−10	82	21	26
−15	55	9	15
−20	48	3	8
−25	56	1	7

The marked effect of slight changes in the reaction of the medium is rendered very apparent by this table. The most favorable reaction is one that is slightly alkaline to litmus, but still requires ten to twenty cc. of normal alkali solution per liter to make it neutral to phenolphthalein. When the acidity is either greater or less than this amount, there is a rapid falling off in the relative numbers of colonies formed.

While it was known for many years before the discovery of the nitrifying organisms, that the presence of some base is necessary to the activity of nitrification, there is very little known in regard to the exact degree of variation that can take place in the reaction of the materials undergoing nitrification without causing an interruption of the process. In the cultivation of the nitrifying bacteria in artificial media, it has been customary to add some carbonate that will neutralize the nitric acid as fast as it is formed. For this purpose, the carbonates of calcium and magnesium have been much more used because they are without influence upon the reaction of the medium until acid has been formed to decompose them. Warington[1] has made some experiments to determine the proportions of sodium carbonate and bicarbonate that can be used for this purpose. He reports that sodium bicarbonate can be used in the proportion of one to four grams per liter, that six grams per liter retards the activity of the ferments, and that eight grams per liter stops it entirely. The use of sodium carbonate was not attended with as good results, since one gram per liter was found sufficient to greatly retard the vigor of nitrification. This is practically all that is recorded in regard to the effect of acidity and alkalinity upon these organisms, except some statements in regard to nitrification in peaty and other soils sufficiently rich in humus to be acid in reaction. It has been reported that some soils of this type contain no nitrates whatever while in place.[2]

There are several ways of testing the effect of acidity upon the nitrifying bacteria. The soil itself may serve as a medium without sterilization, or it may be used after sterilization, the seedings being made from pure cultures of the nitrifying organ-

[1] *J. Chem. Soc.*, *1891*, 59, 529.

[2] Chuard, *Compt. rend.*, 114, 181–184.

isms or from mixed cultures of the soil bacteria; artificial media may be seeded from pure cultures of the nitrifying organisms, from mixed cultures of the soil organisms, or with a small portion of the soil to be studied. Each of these methods has its advantages and uses. In any case, the supply of ammonia must be maintained until the process of nitrification is arrested by the acidity of the medium. When the soil is used as a medium or as the inoculating material, the experiment becomes a test of both soil and organisms, as the acid formed can have no retarding action until all of the readily salifiable base of the soil has been satisfied. When the mixed organisms of the soil are used in media containing organic matter, acid may be produced by other organisms besides the nitrifying bacteria.

As we had some forty samples of soil at our disposal during the last year for other purposes, it seemed wise to improve the opportunity to test the influence of acidity on the nitrifying organisms contained in soils from various parts of the country. The medium selected for this purpose had the following composition:

Ammonium sulphate	0.943 gram.
Dipotassium hydrogen phosphate	1.0 "
Magnesium sulphate	0.5 "
Calcium chloride	trace
Water	1000.0 cc.

One hundred cc. of this solution were used for each test. Before the addition of the ammonium salt, one liter of this medium requires two and six-tenths cc. of normal solution of sodium hydroxide to make it neutral to phenolphthalein. The titration was made without the ammonium salt, as the indicator is not applicable in its presence. As for every equivalent of nitric acid formed during the nitrification of this solution, an equivalent of free sulphuric acid is liberated; the nitrification of fourteen parts per million of nitrogen causes an acidity of the medium equal to two cc. of normal alkali per liter.

A summary of the results of forty-four tests is given in the following table. Twenty-two virgin soils and twenty-two cultivated soils are represented, coming from twenty-two states and territories. The tests were continued for two months and the

figures recorded indicate the maximum number of parts per million of nitrogen nitrified during that time. In five cases no nitrification occurred; in four of these cases no nitrification occurred in the parallel tests made with the same soils and with the same medium to which calcium carbonate was added to neutralize the acid formed. In all but three of the tests the final product was entirely nitrate, showing that the nitric ferment was able to endure at least as much acidity as the nitrous ferment. In the three tests in which the nitrification was incomplete, there was only a small portion of the nitrite remaining unchanged to nitrate.

SUMMARY OF RESULTS.

In	5 cases	0	parts	per	million	of	nitrogen	were	nitrified.
"	1 case	11	"	"	"	"	"	"	"
"	2 cases	14	"	"	"	"	"	"	"
"	4 "	15	"	"	"	"	"	"	"
"	5 "	18	"	"	"	"	"	"	"
"	10 "	20	"	"	"	"	"	"	"
"	5 "	22	"	"	"	"	"	"	"
"	6 "	25	"	"	"	"	"	"	"
"	1 case	28	"	"	"	"	"	"	"
"	1 "	40	"	"	"	"	"	"	"
"	1 "	42	"	"	"	"	"	"	"
"	1 "	70	"	"	"	"	"	"	"
"	1 "	130	"	"	"	"	"	"	"
"	1 "	170	"	"	"	"	"	"	"

Averages:

Of 44 tests 28 parts per million of nitrogen were nitrified.
" 34 " 20 " " " " " " " ,

excluding five cases in which no nitrification occurred and five cases in which it was forty parts per million or more.

Remembering the numbers given above, we notice that the nitrification has stopped after the formation of an acidity equal to three to four cc. normal alkali, or when the reaction reaches five and a half to six and a half of Mr. Fuller's scale. It is quite possible that this extreme sensitiveness to acidity may account for the failure of attempts to grow these organisms upon ordinary peptone jelly.

In the case of the two peaty soils from the muck lands of

Florida, the results were twenty and twenty-two parts of nitrogen nitrified per million, which are very close approximations to the mean result of all the tests. The soils giving the excessive results of 130 and 170 parts per million were from Alabama, and examination has shown that they are both very rich in calcium carbonate. This, of course, explains the high results obtained.

We have "stock cultures" of the nitrifying organisms of all of these soils and hope to be able to report a repetition of these experiments with pure cultures, thus eliminating possible sources of error that may have resulted from the presence of the basic substances of the soils used as inoculating material in the series just reported. It is also desirable to determine the relative effects of various organic and inorganic acids upon the nitrifying organisms. This can only be satisfactorily accomplished by use of pure cultures. In regard to the effect of acidity upon the nitric ferments, but very little is known, except that, as we have observed above, they are not more sensitive to acidity than the nitrous ferments. The practice seems to have been to add an insoluble carbonate to the liquid media used for the growth of nitric organisms also, but we have found that this is unnecessary. The nitric organisms from all of the soils with which we have experimented, thrive well in a medium having the composition of the one given above in which sodium nitrite takes the place of the ammonium salt. There is, of course, no increase in the acidity of the medium during the growth of this ferment, as it merely changes nitrites to nitrates.

The organisms coming from various parts of the country seem to be very uniform in regard to their ability to endure acidity. If these results are again obtained when the tests are repeated with the pure organisms isolated from the different soils, the interpretation to be given to them is a very important one: these results are to be looked upon as evidence that we are to seek practical results in the study of the nitrifying organisms, not from a search for a peculiarly active species, but from a search for those conditions that are most favorable to the activity of these organisms in any given set of soil and climatic conditions.

These conclusions gain strength from the results of the recent

experiments of Burri and Stutzer,[1] in which they found that the mixed organisms from several samples of soil from widely separated sources assumed an almost constant nitrifying power after a series of cultivations in an artificial medium. Whether their results are to be interpreted as an evidence of constant nitrifying power in organisms from widely different soils when these organisms are cultivated in the same medium, or whether they are to be regarded only as another example of the extreme variability that bacterial species have so often been observed to exhibit, is only to be determined by extended experiments. Of high value for the confirmation of these, or of any other results obtained by means of artificial culture medium, is the re-inoculation of several soils with each of the organisms studied, noting the results during long periods of time. Both sterilized and unsterilized soils should be used for this purpose, as well as soils in which the chemical and biological conditions have been variously modified by artificial means.

We feel that the contribution that we have just made to the knowledge of this subject is almost lost in the vast unknown of the field that still remains to be explored, but this is offered as a note of the work that has been undertaken by us of attempting to make a comparative study of the microorganisms important to agriculture in typical soils from all parts of the United States. This note is not presented with any desire to preempt this field of study, for it is broad enough to monopolize the time and skill of many workers for many years to come.

STANDARD PRISMS IN WATER ANALYSIS AND THE VALUATION OF COLOR IN POTABLE WATERS.

BY ALBERT R. LEEDS.

Received April 16, 1896.

IN one of the first papers read before this Society and contained in its Proceedings, Vol. II, p. 1, for 1878, I have given an account of an instrument and a method for reading the quantities of ammonia obtained in nesslerizing, the instrument being termed a color comparator. It was designed primarily for this purpose only, and had its origin in the irregularities observable

[1] *Centralblatt f. bakteriologie u. Parisitenkunde*, *1896*, 2, 105-116.

in the readings of the very minute amounts of ammonia obtained in the course of water analysis. It was subsequently found to be of great service in giving more precision to the measurement of color in potable waters, and it was used for this purpose and also for the estimation of the percentage of carbon in pig-irons, etc. The color struck by 0.01 milligram of ammonia was taken as the unit for natural waters.

The apparatus has been figured in the catalogues of the dealers for the past twenty years, and I need not describe it again here. It avoided the sources of error due to reading the tubes under different conditions and from the side, from the top and in different manners.

The light was reflected from a mirror, placed at an angle of 45°, down and through the middle of the tubes standing on the rack, and then by a second mirror placed below, but at right angles to the first, outward to the eye of the observer. The object was to compare the colors obtained in nesslerizing not with any one series of trial tubes prepared at the time and which might vary within wide limits, but with a coloring material contained in a wedge in connection with which the results of many readings could be plotted and so preserve a permanent standard of comparison. This wedge was placed below the aperture, next to the tube under comparison, but in order that the optical image might be similar in all respects, a tube filled with distilled water was placed above the wedge and the dark rings made by the light transmitted downward through the walls of this tube, made a part of the image also.

All that the eye then had to do was to determine whether the depth of color in two rectangular spaces, as seen in the lower mirror, each space being twenty-five mm. by ten mm. and separated by an interval of ten mm., was or was not equal. When the rack is full, which is the case in two duplicate nesslerizings, the whole of the results are before the eye of the observer at one and the same time, and twelve blocks of color strung along one after another in a horizontal line, are seen brilliantly lit up on a perfectly black ground.

But the difficulty was to obtain a suitably colored fluid to fill the prism. Naturally enough recourse was had in the first place

to the chromogenic metallic salts as being easiest to prepare of a definite strength, and as probably of the most permanent composition. To this end very many trials were made with mixtures of iron, chromium, nickel, cobalt, ferrocyanogen, gold and platinum, but all without success. When a solution gave a series of tints which were satisfactory for the lower end of the scale, it was unsatisfactory for the upper, and vice versa. Then mixtures of these salts with admixtures of coloring matters and with infusions of tea, coffee, etc., were tried and finally a solution of caramel corrected by anilin red showed as close a parallelism with the colors struck by the nesslerized ammonia as any combination experimented upon.

It was fully recognized at the time that none of these expedients fulfilled the conditions of complete parallelism of tint, permanence and ease of handling, that were desirable, and the attempt was made to substitute for the hollow wedge one of colored glass. Mr. Emil Greiner obtained many specimens of greenish-yellow, yellow and orange-yellow glass, and lent his skill in grinding them down into suitable long thin prisms. But they all failed at one or the other end of the scale, and when they were examined by the spectroscope and the difficulty was found to be due to a selective absorption of the color in the different parts of the prism, the attempt to make a satisfactory prism out of one kind of glass only was abandoned. Then thin sheets of differently colored glasses were taken, with the hope that by combination and superposition the changes of tint throughout the scale could be imitated. But at this time a very limited number of shades of color in glass could be obtained. At the present day, with the enormous development of the art of making and using glass for decorative purposes, the case is different. I am experimenting upon composite wedges, made up of wedges of different colors, and the results are promising. Certainly the obstacles to be overcome are not nearly so great as those which have been surmounted in getting rid by means of over-correction and under-correction of both spherical and chromatic aberrations in a lens. Similar composite glass wedges could be employed to estimate minute amounts of iron when a color reaction with a thiocyanate or ferrocyanide is utilized, or for

small quantities of copper or other color-giving substance.

We are only too familiar with the sources of error in the Nessler process, and every chemist at the outset of his work in water analysis is compelled to devote much time to their study. A very slight variation in the mode of preparation makes a great difference in the sensitiveness of the Nessler reagent itself. Potassium, mercury, chlorine and iodine form a large number of salts, and that their molecules are complex and constantly changing is shown by the gradual change of color of the reagent from its first pale greenish-yellow color to a light straw tint with a corresponding gain in sensitiveness. But even with a reagent which is duly sensitive in the lowest part of the scale, and with due care in seeing that the liquids are brought to a proper temperature, and with every minute precaution as to measurements, thorough admixture, etc., there still remains many uncontrollable irregularities. It frequently is the case that the color struck by 0.001 milligram of ammonia is even greater than that given by 0.002 milligram; that given by 0.002 about the same as that given by 0.003, and so on. On standing, the precipitates which settle out, are not uniform in composition, red tetragonal crystals, resembling mercuric iodide, being oft-times accompanied by dark green crystals resembling the mercurous salt. By making up a sufficiently large number of trial sets at one time, it is possible to pick out from them a series in which the differences of tint corresponding to five-tenth cc. of ammonia are, so far as the eye can judge, equal.

The same result is obtained by plotting the results of many readings on a permanent scale. As ascertained by comparison with such a scale, the sum totals of the readings are more accurate than those obtained by comparison with any one trial set made up of fluctuating and perishable members. When we consider that there is an increase both in the delicacy of the reaction and in the ability to read the color tint up to a maximum, after which both fall away again, it is probable that the most accurate method of reading would be to have a permanent scale, divided into equal parts, and to use the scale only for so much ammonia as corresponds to the differences of color which the eye is capable of estimating with certainty.

VALUATION OF COLOR.

As has been remarked above, it was not till after the color comparator had been proposed as a means of estimating the percentage of nesslerized ammonia, that the same scale was extended to the measurement of color in waters. The article in the Journal was reprinted with illustrations in the *Zeitschrift für analytische Chemie*, 17, *276*, and in the *Chemical News*, in the issue of June 7, 1878. In the issue of the latter journal for April 14, 1881, in their report upon the London water supply, Crookes, Odling and Tidy gave the following account of a similar method:

"For some time past we have been experimenting on methods of determining the colors of water, and we have this month adopted a process which, whilst it does not pretend to absolute accuracy, is a great improvement over the arbitrary 'degrees of tint depth' by which the color of water has hitherto been estimated. The process briefly is as follows:

"Two hollow wedges are filled, one with a brown and the other with a blue solution,[1] and these are made to slide across each other in front of a circular aperture in a sheet of metal. In this way any desired combination of brown and blue can be produced. Each prism is graduated along its length from one to forty, the figures representing millimeters in thickness of the solution at that particular part of the prism.

"On a level just below the prisms is a two-foot tube containing the water under examination, and having in front of it a circular aperture of the same size as the one in front of the prisms.

"The stand supporting the prisms and tube is placed horizontally in front of a uniformly lighted window. The observer, standing a little distance off, sees two luminous disks, the lower one illuminated by light, which has passed through two feet of water, and the upper one illuminated by light which has passed through the respective thicknesses of the brown and blue solutions.

[1] The solutions are made in the following way: *Brown Solution*. Dissolve ferric chloride and cobalt chloride in distilled water in such proportion that one liter of the solution contains 0.7 gram of metallic iron, and 0.3 gram of metallic cobalt. A very slight excess of hydrochloric acid must also be present. *Blue Solution*. Dissolve ten grams of pure crystallized copper sulphate in one liter of distilled water.

"By sliding the prisms sideways, one way or the other, it is easy to imitate with considerable accuracy the depth and tint of the color of the lower disk. A metal pointer affixed over the center of the upper disk shows on the prism scales the number of millimeters in thickness through which the light has passed to produce a color which corresponds to that of the water, and the results are recorded in the following way: Brown : Blue. Thus: "February 21, (New River), 20 : 21 means that on that date the color of New River water seen through a two-foot tube was represented by twenty millimeters of brown and twenty-one millimeters of blue solution."

Subsequently the board of London examiners abandoned the use of iron and substituted for it one of potassium dichromate.

Recently Allen Hazen, in the March number of this Journal, has advocated the use of a solution of platinic chloride, this constituent being of fixed strength, together with a solution of cobalt chloride to be added in accordance with the color sense of the observer. Possibly other chemists are employing still different solutions, and it is probably somewhat premature to expect at the present moment a concensus of opinions as to the best substances to be employed. In laying out the methods to be pursued in the examination of the waters submitted to the State Board of Health of Massachusetts (see their Report for 1890), T. M. Drown adopted the Nessler ammonia scale as the scale for color also. And in the January number of this Journal, E. H. Richards has given at length the reasons for adhering to this scale and her method of applying it through an intermediate set of colored natural waters, verified by fiduciary comparisons of certain points on the Nessler ammonia series.

In order that this renewed discussion may have the greater practical value, I shall venture to make the following suggestions:

1. That the unit of depth in the measurement of the color of water should be taken at 200 mm. This depth was used in the comparison tubes, which contain 100 cc. at the 200 mm. mark, for the reason that the same depth has already been adopted in the polariscope. Moreover, 200 mm. or eight inches, is a depth of water familiar in household use, while two feet is not, and

it is a unit that can be more conveniently applied to the unfiltered surface waters now in general use in this country, than the two-foot depth made necessary in gauging the filtered waters supplied to London and other European cities. With the general introduction of filtered waters in this country, three times 200, or 600, (which is very nearly two feet), could be used in measuring color in water that fell below 0.2° on the scale. The unit tube could be applied to waters showing between 0.2° and 2°. In order to preserve identity of conditions, which is of such fundamental importance in optical measurements, instead of diminishing the depth of the more highly colored waters, those between 2° and 4° could be diluted with an equal bulk of water and read in the unit depth of tube.

2. I would respectfully urge as a matter of priority and inasmuch as a very great number of measurements of color in this country are already so recorded, that the unit therein adopted which corresponds to the color struck by 0.01 milligram of nessnerized ammonia, should be retained. It may be said that for the reason already given this unit is one which cannot be precisely ascertained. But to compare lesser things with greater the same thing may be said of the meter; to rectify it in the manner originally intended, will prob bly never be attempted, and yet, at the same time, the meter is an universally accepted and well defined magnitude. Moreover, every time an ammonia determination is made, this unit must be ascertained and the readings for color are usually done at the same time as those of ammonia. Whether a scale is made with chromium or platinum or any other pure substance, there would be no difficulty in determining the weight of metal to be used to give the same color as that struck by 0.01 milligram of ammonia, within any such limit of precision as the eye is capable of measuring. Such a scale divided from 0 to 1 into ten equal parts and then the same divisions continued higher, could be used in the estimation of ammonia also.

3. Instead of using this scale directly, there would be great gain in using its equivalent in glass. If he desired, each chemist could test the glass scale by comparison with a fluid one made

by himself, but in daily use indestructable and properly compensated glass wedges have many advantages.

A METHOD FOR SEPARATING THE "INSOLUBLE" PHOSPHORIC ACID IN MIXED FERTILIZERS DERIVED FRON BONE AND OTHER ORGANIC MATTER FROM THAT DERIVED FROM ROCK PHOSPHATE.

BY A. P. BRYANT.

Received April 13, 1896.

DURING the year 1895 the wholesale price of rough bone was about \$19.50 per ton in the New York markets. Ground bone brought \$22.75 per ton, and ground Charleston rock averaged \$8.12½ per ton. After allowing for the value of the ammonia, the phosphoric acid purchased in bone still costs considerable more than the same amount purchased in mineral phosphates.

Estimating 3.75 per cent. of nitrogen in the ground bone, wholesale cost 12.3 cents per pound, there would be \$9.23 worth of nitrogen per ton. This value would make the phosphoric acid in a ton of ground bone cost at wholesale \$13.52, when the same amount approximately of phosphoric acid in ground rock costs about \$8.12½ per ton.

This cheapness of mineral phosphates has led to their very general use by fertilizer manufacturers instead of bone as a source of phosphoric acid.

While the so-called Available Phosphoric Acid[1] of the two may be of equal value, it seems wrong to classify the phosphoric acid of mixed fertilizers insoluble in the ammonium citrate solution at the same price in the two. The Connecticut State Station's Report "Trade Value," of the organic phosphoric acid is (average) five cents per pound, while in the raw ground rock it is but two cents per pound.

It has been urged that there is no means of telling whether the "insoluble" phosphoric acid in mixed fertilizers was derived from minerals, or from bone and tankage. It was for

[1] That portion soluble in a neutral solution of ammonium citrate, sp. gr. 1.09, digested at 65° C. for thirty minutes.

this reason that the experiments herewith described were undertaken.

The method employed depends upon the difference in specific gravity between bone and other organic matter and the mineral phosphates. The following are the specific gravities of some of the more important compounds found in bone and in rock phosphates :

	Sp. Gr.
Bone and other organic matter, less than	2.0
Gypsum	2.3
Aluminum phosphates	above 2.3
Iron phosphates	about 2.6
Silica	2.65
Calcium phosphates	2.9 to 35.5
Fluorite	3.2

For the separation of the bone and organic matter from the mineral matter, a solution of mercuric iodide in potassium iodide was employed. This solution was first proposed by E. Sonstadt[1] in 1873, and elaborated by Thoulet[2] in 1878. The solution, as prepared by the writer, is as follows: Seventy-five grams of potassium iodide are dissolved in 350 cc. of warm water, and 100 grams of mercuric iodide added. The solution is filtered and evaporated in a porcelain dish over a water-bath, until a crystal of pure gypsum, sp. gr. 2.3, comes to the surface. The solution is then diluted at 15.5° C. until the gypsum is of the same density as the solution, scarcely floating or sinking. The solution is now at specific gravity 2.3, and should be diluted to specific gravity 2.26 according to the formula $V' = \frac{V(D-D')}{D'-1}$ where V' is the volume of water to be added, V the volume of the solution, D its specific gravity 2.3, and D' the desired specific gravity 2.26. The specific gravity should be verified by use of the picnometer.

The separating solution should be placed in a small flask of about 100 cc. capacity, fitted up on the same plan as a wash bottle. The amounts given above will make about 100 cc. of solution.

[1] *Chem. News*, 29, 127.
[2] *Compt. Rend.*, Feb. 18, 1878.

The tube for making the separation may be as elaborate as desired. A very good form is described by S. L. Penfield in the *American Journal of Science* for Dec. 1895. The following has given excellent satisfaction in these experiments. A glass tube, a broken burette for example, about one and three-tenths cm. internal diameter and twenty cm. long is connected by means of a short piece of rubber tubing, with a tube of similar diameter, closed at one end and about seven cm. in length. See Fig. 1.

The material to be separated is placed in the tube and fifteen or twenty cc. of the separating solution added, after which the tube is stoppered and shaken thoroughly. The sides of the tube are now washed down with more of the solution; after standing for five minutes, the bottom part or bucket should be tapped smartly to release any light portions carried down with the heavy material, and a jet of the solution blown against the matter floating at the top, to dislodge any heavy particles. The tube is then let stand till the solution is clear, all matter having gone to the top or bottom. This will usually take from forty minutes to an hour in finely ground mixed fertilizers or rock superphosphates.

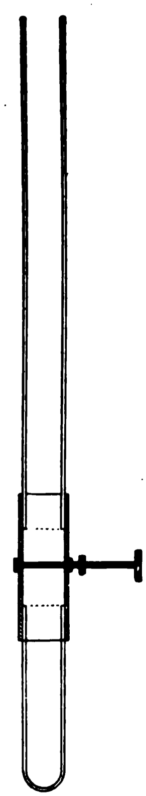


Fig. 1.

The rubber tube is now tightly clamped with a screw pinch-cock, separating the heavy material from the light. A beaker is placed beneath the tube, and the lower tube or bucket is removed, the fingers being encased in rubber finger-tips, as the separating solution cracks the skin. The tube and contents are brought on a dry filter and the liquid filtered back into the supply flask. Water is then used, the first washings being saved and evaporated down to a specific gravity of 2.26 again. The light portion is treated in a similar manner, care being taken to get all particles out of the tube at the last.

At first it was not supposed necessary to have any fixed specific gravity, but as will be seen by the following table, it is

important that the specific gravity should be somewhere about 2.26. The exact reason for this is not in the province of this paper to decide, but seems to be owing to the low specific gravity of the aluminum phosphates.

The plan of the experiments carried on was to take a fertilizer known to contain nothing but organic matter as a source of phosphoric acid, and a mixture of South Carolina and Florida phosphates, both the raw rock, and the acidulated product. These were analyzed and then mixed in different proportions and treated with the separating solution.

In the first experiment two grams of the mixture were treated with 100 cc. of the the neutral ammonium citrate solution (sp. gr. 1.09), and digested for thirty minutes at 65° C., shaking every five minutes. After filtering, the dried insoluble residue was separated as carefully as possible from the filter paper and treated as previously described. As will be seen by reference to the table following, this method, though most desirable, was given up owing to the large proportion of phosphoric acid left on the filter paper.

The next attempt was to treat the mixed fertilizer directly with the separating solution, and was also abandoned owing to soluble matter in the fertilizers which destroyed the separating solution.

These two experiments showed two things clearly, that the fertilizer cannot be treated with ammonium citrate solution before separating, and that the matter soluble in water must be removed before separating.

To obtain this latter end and expose the minimum amount of filter paper, the inner tube of a fat extraction apparatus was used, such as was described by Prof. S. W. Johnston.[1] These tubes are used by the Storrs (Conn.) Agricultural Experiment Station, and are made for them by Whitall, Tatum & Co., New York. The tube is about fifteen cm. in length and two and five-tenths cm. internal diameter, slightly contracted at one end, which has a rim so that a piece of filter paper reinforced on the outside with cheese cloth, can be tied on. (Fig. 2.) The method is as follows :

[1] *Am. J. Sci.*, **13**, 190, *1877*

Two grams of the raw or mixed fertilizer are transferred to the "extraction" tube and extracted with nearly 250 cc. of hot water, as for water soluble phosphoric acid determination. The tube and contents are placed in a drying oven, and when thoroughly dry the filter paper is taken off and all matter carefully removed with a spatula and brush. Any fine sediment adhering to the glass may be removed by a rubber tipped glass rod.

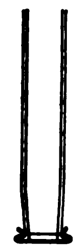


Fig. 2.

The material is now transferred to the separating tube and treated as before described.

The light portion and heavy portion are treated separately with ammonium citrate solution, and the insoluble phosphoric acid determined in the usual way. That in the "light" comes from bone, tankage or other organic matter, that in the "heavy" from minerals.

The following is a tabular statement of the results of the experiments:

Material.	Total P_2O_5.	Insoluble P_2O_5.
Prepared mixed fertilizers[1]	10.75	2.56
Mixed Florida and Carolina raw rock......	27.51	24.36
Mixed Florida and Carolina dissolved rock.	16.23	0.77

PERCENTAGE OF PHOSPHORUS PENTOXIDE FOUND IN THE HEAVY AND LIGHT PORTIONS AND LEFT ON THE FILTER PAPER.

No. of experiment.		Specific gravity.	Light. Theoretical.	Light. Found.	Heavy. Theoretical.	Heavy. Found.	Left on paper.	Total. Theoretical.	Total. Found.
	Treated with ammonium citrate before separating.								
1	Mixture A 1	2.46	1.28	1.79	12.18	8.33	2.66	13.46	12.78
2	Mixture B 2	2.46	1.28	2.02	0.39	0.43	0.44	1.67	2.89
3	Mixture A 1	2.46	1.28	1.83	12.18	8.33	2.66	13.46	12.82
4	Mixture A 1	2.35	1.28	1.52	12.18	9.68	2.66	13.46	13.86
5	Mixture B 2	2.35	1.28	1.66	0.39	0.49	0.44	1.67	2.59
	Separated before treating with ammonium citrate.								
6	Mixture B 2	2.22	1.28	0.93	0.39	0.70	trace	1.67	1.63
7	Mixture A 1	2.26	1.28	1.38	12.18	11.65	0.12	13.46	13.15

[1] Containing acidulated bone, tankage, dried blood, sodium nitrate and potassium sulphate.

No. of experiment.		Specific gravity.	Light. Theoretical.	Light. Found.	Heavy. Theoretical.	Heavy. Found.	Left on paper.	Total. Theoretical.	Total. Found.
8	Mixture C 3	2.26	1.28	1.63	6.28	6.03	0.06	7.56	7.72
9	Mixture B 2	2.26	1.28	1.18	0.39	0.65	trace	1.67	1.83
10	Mixture A 1	2.26	1.28	1.28	12.18	12.03	0.12	13.46	13.43
11	Mixture C 3	2.26	1.28	1.35	6.28	6.08	0.06	7.56	7.49
12	Mixture B 2	2.26	1.28	1.11	0.39	0.48	trace	1.67	1.59
13	Mixture A 1	2.26	1.28	1.24	12.18	12.07	0.12	13.46	13.43
14	Mixture C 3	2.26	1.28	1.15	6.28	6.09	0.06	7.56	7.30
15	Pre'd mixed fertiliz'r	2.26	2.56	2.51	....	....	trace	2.56	2.51
16	Dissolved rock......	2.26	...	...	0.77	0.70	trace	0.77	0.70

1 Mixture A, 1.0 gram prepared mixed fertilizer.
" " 1.0 gram raw Florida and Carolina rock.
2 Mixture B, 1.0 gram prepared mixed fertilizer.
" " 1.0 gram dissolved Florida and Carolina rock.
3 Mixture C, 1.0 gram prepared mixed fertilizer.
" " 0.5 gram raw Florida and Carolina rock.
" " 0.5 gram dissolved Florida and Carolina rock.

Of the above analyses, the first five were tentative, the method and manipulation were experimental, and the results were unsatisfactory. They show, however, that a specific gravity of 2.46 or 2.35 is too heavy for the proper workings of this method, and that when treated with ammonium citrate solution before separation, at least twenty per cent. of the phosphoric acid is lost through the adherence to the filter paper.

The sixth analysis shows that a specific gravity of 2.22 is too light, and matter which should rise to the top sinks to the bottom. Nos. 7 to 14 show that the method as finally elaborated, is quantitative and apparently reliable and capable of being put into regular use as a method of testing the source of the insoluble phosphoric acid in mixed fertilizers. The attempt was made to treat first with ammonium citrate, and filter through the extraction tube above described, in order to expose less filter paper, but the solution would not filter at all.

No. 15 was a sample of mixed fertilizer containing acidulated bone, tankage, dried blood, sodium nitrate and potassium sul-

phate, and formed the source of the "light" phosphoric acid in the above experiments. When treated with the separating solution (after dissolving out salts soluble in water) everything rose to the top with the exception of a very small amount of some material, either calcium sulphate or silica, as there was no trace of phosphoric acid in it. The solution was perfectly clear in ten minutes.

No. 16 was the acidulated Carolina and Florida rock used in the above experiments. When treated with the separating solution, a small amount came to the top. There was, however, no trace of phosphoric acid in this portion. It took an hour for the solution to become clear, showing the presence of some substance, probably calcium sulphate and aluminum phosphates, of specific gravity but little higher than that of the solution, namely, 2.26.

The method of analysis were those of the Association of Official Agricultural Chemists.

SUMMARY.

The following method is proposed for separating the insoluble phosphoric acid in mixed fertilizers derived from bone, tankage or other organic matter, from that derived from mineral phosphates.

SOLUTIONS AND APPARATUS.

Separating Solution : Seventy-five grams of potassium iodide and 100 grams of mercuric iodide are dissolved in 350 cc. water and evaporated over a water-bath to a specific gravity of 2.26. This solution should be kept in a small flask arranged like a wash bottle.

Other solutions necessary to determine available and total phosphoric acid.

Separating Tube : Two tubes one and three-tenths cm. internal diameter, one seven cm. in length, closed at one end, the other twenty cm. long. These are connected by a piece of stout rubber tubing, so that the lower part or bucket, can be separated by a screw pinch-cock from the upper portion.

Extraction Tube : A tube two and five-tenths cm. internal

diameter, slightly contracted at one end, which has a rim over which filter paper and cheese cloth can be tied.

Other apparatus as for available and total phosphoric acid determinations.

Manipulation: Two grams of the substance to be examined are transferred to the extraction tube and washed with from 100 to 225 cc. of hot water, depending upon whether or not water soluble phosphoric acid is to be determined. Dry thoroughly, remove substance carefully, using spatula, brush, and rubber tipped glass rod, and transfer to a separating tube. Add fifteen to twenty cc. of the separating solution, shake thoroughly and wash down the sides of the tube with a jet of the solution. After standing five minutes tap the lower part or bucket smartly with the finger, to release any light portion carried down with the heavy, and stir up the matter on top with a jet of solution.

Let stand until the solution is clear, or for one hour, clamp the rubber tube, place a beaker under the bucket, which is carefully removed, the fingers being encased in rubber finger tips. Filter the solution back into the supply flask, wash thoroughly, saving the first washings for evaporation to a specific gravity of 2.26 again, and treat for insoluble phosphoric acid in the usual way. The light portion is treated in a similar manner. If desired, the heavy and light portions can be treated as for total phosphoric acid, thus determining all of the phosphoric acid derived from inorganic and organic sources respectively, except the water soluble.

MIDDLETOWN, CONN.

SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.[1]

BY GEORGE AUCHY.

Received April 16, 1896.

VOLHARD'S method of determining manganese is generally considered a very accurate one; nevertheless, that the

[1] In this Journal, 18, 406, I omitted to state a precaution used, in the manner of performing Drown's sulphur method there described. The solution from the Troilius' bulb is heated to boiling (preferably with the previous addition of permanganate solution) before filtering into it the hydrochloric acid solution from the graphitic residue. This is to oxidize any sulphur that may be present as sodium sulphide.

accuracy of the process is strictly dependent upon certain conditions and precautions not pointed out by the author, and not generally recognized (so far as the writer is aware) seems proved by the experience with the method and with Stone's modification of it, which follows :

STONE'S MODIFICATION.

Mr. Geo. C. Stone makes a very considerable saving in time by omitting the evaporation with sulphuric acid, and precipitating the iron immediately with zinc oxid as soon as solution of the drillings in nitric acid is effected.[1] But in Volhard's original article, as also in Blair's Chemical Analysis of Iron, it is directed to destroy the carbonaceous matter by evaporation to dryness and strongly heating, or by evaporation with sulphuric acid till fumes of the latter come off, and as previous to the appearance of Mr. Stone's paper the writer, on testing this point by dissolving in sulphuric acid with enough nitric added to oxidize the iron and help effect the solution of the drillings and omitting the evaporation, had obtained results several hundredths higher (although Volhard's objection to organic matter is that it hinders the balling together of the manganese dioxide in titration) than those obtained from the same samples by the regular process, it was judged that this precaution was not a useless one ; and after reading Mr. Stone's article it was therefore considered well, as a precaution, to test his process also in this particular, and for that purpose the following determinations were made :

TABLE I.

No.	Carbon. Per cent.	Volhard's method. Per cent.	Stone's modification. Per cent.
476	0.585	0.46	0.53
495	0.80	0.57	0.65
503	0.228	0.423	0.45
505	0.225	0.49	0.52
483	0.17	0.43	0.51
486	0.185	0.54	0.61
507	0.315	0.44	0.44

[1] This Journal, 18, 228. Mr. Stone finds that hydrochloric acid solution also works well.

The results of Stone's method were very considerably higher than those by the regular method, except in the case of 507. But in the case of 507 it was noted that in making the precipitation of the iron by the zinc oxide a large excess had been accidentally used, while in all the other determinations the zinc oxide had been added in amount sufficient to precipitate the iron merely; and it was therefore thought advisable to see whether the considerable differences in the results by the two method's—Volhard's and Stone's—was not due to this fact (insufficient neutralization in the latter) before attributing it to the organic matter undestroyed in Stone's method. The above determinations were therefore repeated, using in each case not only enough zinc oxide to coagulate the solution and precipitate the iron as directed, but also enough in excess of this amount to turn the brownish red color of the iron precipitate to a light brown. The results follow:

TABLE II.

No.	Carbon. Per cent.	Volhard. Per cent.	Stone. Zinc oxide to coagulation. Per cent.	Stone. Zinc oxide in large excess. Per cent.
503	0.228	0.423	0.45	0.45
505	0.225	0.49	0.52	0.51
483	0.17	0.43	0.51	0.45
483	0.17	0.43	0.51	0.45
486	0.185	0.55	0.61	0.58
486	0.185	0.54	0.61	0.58
476	0.585	0.46	0.53	0.47
495	0.80	0.57	0.65	0.60
471	0.105	0.38	....	0.40
480	0.10	0.35	....	0.36
493	0.57	0.46	....	0.47
507	0.315	0.435	....	0.44
153	0.50	0.64	....	0.70
153	0.50	0.64	....	0.67
153	0.50	0.64	....	0.69
155	0.40	0.56	....	0.56

These results show that when the zinc oxide is added merely to coagulation and precipitation of the iron, leaving the solution probably faintly acid, the manganese is afterward precipitated, not according to the theoretical formula, but with result too high;

and that to insure the correct precipitation of the manganese it is necessary to add the zinc oxide in large excess, so that the solution is thoroughly neutralized when titrated.

It will, however, be noted that with this precaution, observed results in the table are nevertheless a few hundredths per cent. higher than by Volhard's method.[1] Is this difference due to the undestroyed carbonaceous matter? It was thought probable, but to make sure, some of the tests were repeated with oxidation of the carbonaceous matter by addition of lead dioxide to the boiling nitric acid solution of the drillings (the excess destroyed by ferrous sulphate and the excess of the latter oxidized by continued boiling of the nitric acid solution).[2] These results should be lower if carbonaceous matter has any influence. They were not lower, as the following table shows, and hence it is indicated that carbonaceous matter does not interfere. It is true that in one case (483) the result obtained by oxidation of the carbonaceous matter is lower, but the reason for this will appear later on.

TABLE III.

No.	Carbon. Per cent.	Stone. With carbon not oxidized. Per cent.	Stone. With carbon oxidized. Per cent.
480	0.10	0.36	0.37
507	0.315	0.44	0.44
155	0.40	0.56	0.55
155	0.40	0.56	0.57
155	0.40	0.56	0.56
155	0.40	0.56	0.56
153	0.50	0.70	0.68
483	0.17	0.45	0.41

Since the slightly high results obtained by Stone's method, in Table II., are not due to the undestroyed carbonaceous matter, they must be due to the fact of titration in nitric acid solution. The following determinations of manganese in solutions containing no organic matter, and in which the amount of mangan-

[1] It was later seen that the accuracy of the regular Volhard process was also dependent upon certain conditions; and the results by this method, given in these two tables, are the corrected results obtained later by checking with the color method according to Table VI. So that in Tables I. and II. the comparison is really with the color method rather than with Volhard's method. As explained under Table VI., there was not enough left of the samples for gravimetric tests. For a comparison of Stone's method with the gravimetric see Table XI.

[2] The lead dioxide and the ferrous sulphate used were tested for manganese.

ese was known (made by taking definite amounts of standard permanganate solution) are confirmatory of this conclusion :

TABLE IV.

No.	Manganese taken.	Manganese found.	No.	Manganese taken.	Manganese found.
	Per cent.	Per cent.		Per cent.	Per cent.
1	0.40	0.41	8	0.40	0.42
2	0.40	0.41	9	0.80	0.81
3	0.40	0.41	10	0.80	0.82
4	0.40	0.41	11	1.20	1.24
5	0.40	0.41	11	1.20	1.22
6	0.40	0.41	13	0.80	0.81
7	0.40	0.42	14	1.20	1.22

Here, then, is a second precaution to be observed in Stone's method : a correction of the result by one or two hundredths per cent. must in each case be made. But still other precautions are necessary, as will appear.

VOLHARD'S METHOD.

The fact brought out by working upon Stone's method, that titration in faintly acid (nitric) solution gives too high results led to the suspicion that the same was also true of Volhard's regular method (sulphuric acid solution). The following tests were made :

TABLE V.

No.	Volhard. Zinc oxide added to coagulation.	Volhard. Zinc oxide in large excess.
490	0.49	0.39
490	0.49	0.39
490	0.49	0.39
490	0.49	0.49
476	0.51	0.46
507	0.49	0.44
483	0.45	0.41
503	0.45	0.41
471	0.41	0.38
289	0.42	0.40
289	0.42	0.40
493	0.51	0.44
505	0.50	0.46
155	0.58	0.49
155	0.58	0.56
289	0.42	0.41
153	0.66	0.64

Results of the first column were obtained by adding zinc oxide till the solution stiffened and the iron all precipitated. In the second column of determinations the zinc oxide was added in sufficient excess of this amount to make the color of the precipitated iron a light brown. The differences in the results were supposed to be due to this fact already noted in considering Stone's method—that titration in slightly acid solutions gives too high results. But a suspicion arose that these differences might, in part at least, be due to manganese being mechanically carried down with the iron when the large excess of zinc oxide was used. The obvious test of this would have been to make gravimetric determinations in the samples used in the last table. But, unfortunately, there remained but very little drillings of each of the samples. So the next best thing was done, and a standard manganese sample was prepared, and the determinations of these samples of the last table made by the color method: in each case making a number of tests and taking the average. Results:

TABLE VI.

No.	Volhard. Zinc oxide to coagulation.	Volhard. Zinc oxide in large excess.	Color method.
490	0.49	0.39	0.48
507	0.49	0.44	0.435
483	0.45	0.41	0.43
503	0.45	0.41	0.423
471	0.41	0.38	0.38
289	0.42	0.40	0.40
492	0.51	0.44	0.46
503	0.50	0.46	0.49
155	0.58	0.49	0.56

Showing that when the neutralization with zinc oxide is carried only to the point of precipitating the iron the result will invariably be from 0.01 per cent. to 0.05 per cent. too high; while on the other hand, if the zinc oxide be added in excess of this amount, the result *may* be too low, and very much too low from the precipitation of manganese with the iron. These points would have been more certainly and satisfactorily proved, however, had the comparison of the Volhard results been made directly with results by the gravimetric process instead of by the

color test. In the following table such comparisons with the gravimetric method—in a new lot of steels—are made, and confirm the conclusions drawn from the preceding table. In the second column of tests, the neutralization was performed in a way not to precipitate the manganese. In the third column of tests, neutralization was purposely performed in a way most favorable to the precipitation of manganese with the iron.

TABLE VII.

No.	Zinc oxide to coagulation. Per cent.	Excess of zinc oxide. The excess added after filtration of ferric oxide. Per cent.	Excess of zinc oxide. Added suddenly to the iron solution. Per cent.	Gravimetric method. Per cent.	Color method. Per cent.
451	0.56	0.51	0.51	0.52 (acetate)	0.53
452	0.46	0.44	0.44	0.43 "	0.435
453	0.46	0.46	0.37	....	0.425
454	0.47	0.47	0.44	0.46 (Ford)	0.45
493	0.51	0.46	0.44	....	0.46
456	0.45	0.41	....	0.41 (Ford)	0.43
466	0.54	0.49	....	0.485 "	0.49
481	0.48	0.45	....	0.455 "	0.46
153	0.66	0.64	....	....	0.64
000	1.30	....	....	1.25[1]	....

Insufficient neutralization gives high results. Complete neutralization *suddenly*, gives low results. Here then is the explanation for the low result of Table III (483); the ferric oxide precipitate had carried down some of the manganese.

The remedy is obvious. It is to carefully avoid an excess of zinc oxide at the time of precipitating the iron; adding the necessary excess to the aliquot part of the filtrate from the ferric oxide, taken for titration—filtering off the undissolved zinc oxide before titrating. But this procedure involves considerable extra work. And it does not seem necessary, if certain precautions be taken, to filter off the ferric oxide before adding the excess of zinc oxide. For it is reasonable to suppose that it is the *sudden* addition of the zinc oxide in excess to the rather concentrated solution that carries down the manganese. If the iron be first precipitated carefully by the gradual addition of zinc oxide, avoiding an excess, we have seen that no manga-

[1] Made by Williams, of Boston.

nese is carried down. If now, the solution be diluted, mixed, and the ferric oxide be allowed time to begin to settle, there seems no reason why the further addition of an excess of zinc oxide should then precipitate manganese. That it does not is evidenced by the preceding table, second column of results, last four results, which were obtained in this way. Also all of the determinations by Stone's modification in Table XI.

In the determination of the results of the third column of results in the preceding table, pains were taken to add the excess of zinc oxide as suddenly as possible ; nevertheless, only three out of the five results are low, showing (as also do the results of Table VI.) that manganese is not invariably carried down by such a procedure. In Stone's modification the tendency to a precipitation of manganese with the iron seems less ; for of the numerous results by that method (obtained before the necessity of any precaution in precipitating the ferric oxide was known) only one is low. But in both methods the neglect of the precaution to *thoroughly* neutralize with zinc oxide almost invariably gives results more or less above the truth.

Taught suspicion by the experience thus far had, it was resolved to test every step in the method; and the following determinations were made to see if the temperature of the liquid at the time of neutralization with zinc oxide had any influence upon the result :

TABLE VIII.

Solution heated to boiling with the zinc oxide.			Zinc oxide to cold solution.		
No.	Manganese taken. Per cent.	Manganese found. Per cent.	No.	Manganese taken. Per cent.	Manganese found. Per cent.
1	0.40	0.49	1	0.40	0.40
2	0.40	0.44	2	0.40	0.40
3	0.40	0.43	3	0.40	0.40
4	0.40	0.47	4	0.40	0.40
5	0.40	0.42	5	0.40	0.40
6	0.40	0.41	6	0.40	0.39
Solution merely warm.			7	0.40	0.40
1	1.20	1.22	8	0.40	0.41
2	0.80	0.83	9	0.40	0.40
			10	0.80	0.80
			11	1.20	1.20

These results show that neutralization must be performed in the cold. The writer had always practiced this precaution, though for no well defined reason.

The second series of results in the table also show that there is no tendency to slightly high results, as is the case when titration is done in nitric acid solution (Stone's method).

Volhard, in his article, states that the precipitated manganese dioxide is mixed with protoxide unless some metallic base like zinc oxide, lime, magnesia, etc., be present; and, therefore, in the following experiments on this point it was expected that the results would be poor, since the amount of zinc oxide present was purposely kept as low as possible by making the neutralization first with sodium carbonate, and then cautiously adding sulphuric acid till slightly acid, the slight excess of acid being then neutralized with zinc oxide.

TABLE IX.

No.	Taken. Per cent.	Found. Per cent.	No.	Taken. Per cent.	Found. Per cent.
1	0.40	0.41	4	0.40	0.41
2	0.40	0.42	5	0.40	0.42
3	0.40	0.40			

These results seem to show that this is not a very important source of error. In Särnström's method the point is entirely disregarded.

Five determinations made with five cc. free sulphuric acid (two to one) at time of neutralization with zinc oxide give, instead of the theoretical 0.40 per cent. taken, respectively 0.40 per cent., 0.42 per cent., 0.41 per cent., 0.41 per cent., 0.41 per cent.

With six cc. free acid, 0.40 per cent., 0.41 per cent.

With eight cc. free acid, the results of Table VIII.

SÄRNSTRÖM'S METHOD.

Messrs. Mixer and DuBois recommend this method for iron ores,[1] and give results showing its accuracy. In this method zinc oxide is not used, the neutralization (hydrochloric acid

[1] This Journal, 18, 385.

solution) being effected entirely by sodium carbonate, with care not to add it in greater amount than necessary to precipitate the iron, and the subsequent titration is done without filtering off the ferric oxide thus precipitated. This manner of neutralization leaves the solution not thoroughly neutralized, and from the foregoing results of this article we should expect high results from Särnström's method. The results given by Messrs. Mixer and DuBois are, however, excellent results; and this indicates either that neutralization with sodium carbonate in hot hydrochloric acid solution is not attended with the same phenomena as neutralization with zinc oxide in nitric and sulphuric solutions, or that in the former process there is a greater tendency of the manganese to precipitate with the iron, and that the error from this source counterbalances the error from titrating in faintly acid and hot solution. But the uniform excellence of the results given by Messrs. Mixer and DuBois points to the former as the more likely supposition. The method was briefly tested by taking standard manganese solution. Instead of 0.40 per cent. manganese taken in one case, 0.44 per cent., and in another 0.38 per cent. was obtained. But the test was not a fair one as there was no iron present to give the exact point of neutralization as obtained in the regular working of this method. Ferric chloride should have been added, but none was at hand, and the writer postponed further examination of the method for the reason that (as explained by Messrs. Mixer and DuBois) it is not well adapted to the analysis of steel.

COLOR METHOD.

The color method has no kinship to Volhard's, and its consideration is therefore hardly relevant here. But, nevertheless, as it was found necessary in the course of this work to make determinations by this method for comparison with others obtained by Volhard's method in samples almost used up, it might perhaps be just as well to give these color results in detail, as showing the limits of error in the process when performed by one not an expert in its use.

TABLE X.

No.	First reading. Per cent.	Second reading at a higher dilution. Per cent.		Volhard or gravimetric method. Per cent.	
289	0.40 0.395 0 40	0.40 0.39	0.40	0.40	Volhard.
153	0.63 0.61 0.639	0.64 .... 0.65	0.64	0.64	Volhard.
503	0.552 0.564 0.572 0.543	0.547 0.560 0.586 0.555	0.56	0.56	Stone.
503	0.43 0.426 0.42 0.42	.... 0.416 0.425 0.42	0.423	0.41	Volhard.
505	0.495 0.49 0.485 0.495	0.49 0.48 0.485 0.495	0.49	0.49	Stone.
483	0.44 0.425	0.425 0.425	0.43		
486	0.53 0.54	0.534 0.546	0.54		
471	0.38 0.39	0.37	0.38	0.38	Stone.
490	0.48 0.48	0.48 0.486	0.48		
493	0.438 0.47 0.468	0.445 0.466 0.47	0.46	0.46	Volhard.
507	0.43 0.43	.... 0.44	0.435	0.42	Stone.
466	0.488 0.497	0.472 0.498	0.49	0.485	Gravimetric.
481	0.49 0.50 0.455 0.47 0.446 0.476	0.475 0.49 0.454 0.46 0.446 0.47	0.469	0.455	Gravimetric.
453	0.43 0.416	0.426 0.425	0.425	0.425	Stone.
456	0.449 0.427 0.417 0.416 0.417	0.446 .... 0.42 0.428 0.414	0.43	0.41	Gravimetric.
451	0.545 0.53 0.54 0.52 0.52 0.537 0.535	0.56 0.53 0.54 0.52 0.525 0.545 0.531	0.53	0.52	Gravimetrtc.

The results in the table by Volhard's and by Stone's method were obtained by an observance of precautions given—correction of 0.02 per cent. in results by the latter method, thorough neutralization by zinc oxide, etc.

It will be seen that color method results are quite accurate if a number of color comparisons be made and the average taken. But if only one test be made the variation may occasionally be 0.02 to 0.03 per cent. But in these determinations the boiling was all done over the naked flame. Closer results can perhaps be had by using the calcium chloride bath for this purpose, as directed in Blair's Chemical Analysis of Iron.

RECAPITULATION.

The sources of error, then, in Volhard's process, as indicated by the foregoing experiments, are:

1. The incomplete neutralization by zinc oxide, giving usually high results.

2. The too sudden addition of the necessary excess of zinc oxide, giving frequently low results.

3. The titration in nitric acid solution giving results 0.01 or 0.02 per cent. too high.

4. Neutralization by zinc oxide in hot solution, giving high results.

With regard to the first of these sources of error it may be remarked that Volhard recommends slightly acidifying with nitric acid before titration—to oxidize organic matter. But whatever organic matter may be present capable of being oxidized by nitric acid has already been oxidized, and the organic matter and proto salts present in the sodium carbonate and zinc oxide used for neutralization is best determined by a blank or dummy test, or better by performing the process with a convenient measured amount of standard permanganate decomposed by hydrochloric acid. Besides the error from titrating in faintly acid solution, a further objection to acidifying with nitric acid is that the manganese dioxide precipitated by titration collects as a film on the glass and obscures the end reaction.

Stone's modification is much easier and quicker than the regu-

lar Volhard method; not only because the evaporation to dryness with sulphuric acid is dispensed with, but also, as Mr. Stone points out, because in nitric acid solution the precipitated ferric oxide settles so readily and completely that the filtration from it may be omitted, the clear liquid being decanted from the precipitate. In sulphuric acid solution the precipitated ferric oxide does not settle readily enough for this, and thus considerable time is taken up in making folded filters, and the filter paper used adds appreciably to the expense of the method.

Mr. Stone performs the neutralization entirely with commercial zinc oxide, and this is doubtless the reason that his results have always been satisfactory, and he has noticed no necessity for the precaution of thorough neutralization; for in neutralizing altogether with zinc oxide, in the hurry of every day work one would naturally get a large or a considerable excess of it used, even if not recognizing the necessity for such an excess. And as to the precipitation of manganese with the iron, the work in this article would seem to show that to be an exceptional occurrence with nitric acid solution, although of frequent occurrence in sulphuric acid solution if caution be not used in the neutralization. But as regards neutralization, the writer considers it more advantageous to use sodium carbonate, or common sal soda first, finishing up with zinc oxide emulsion, for sal soda is much cheaper than commercial zinc oxide. But, as before mentioned, the manganese, organic matter, and proto salts in these reagents, if any be present, must be allowed for.

Mr. Stone takes 100 cc. for titration. But 250 cc. is perhaps preferable on the score of greater accuracy. The writer finds it convenient to use permanganate of strength exactly 0.0056, taking always three and three-tenths grams of the drillings for analysis. The reading of the scale on the burette then at once gives the percentages of manganese without calculation, except a division by ten.

For the convenience of those unfamiliar with the process details briefly follow, with the precautions found to be necessary in this article printed in italics. Three and three-tenths grams of drillings. Dissolve in fifty cc. nitric acid, sp. gr. 1.20. Wash

into a 500 cc. measuring flask. Add about two-thirds of the amount of sal soda solution necessary to a complete neutralization. *If not cold, cool.* Add zinc oxide emulsion till solution stiffens, *avoiding an excess.* Dilute to about three-fourths of the capacity of the flask, mix and let stand till the ferric oxide begins to settle. See that the solution is colorless. *Add considerable excess of zinc oxide emulsion.* Mix. Dilute to mark. Insert stopper. Mix. Transfer to dry beaker. Mix again. Let settle, and pour off 250 cc. Titrate in 500 cc. Erlenmeyer flask, (first heating to boiling) with permanganate of strength 0.0056. Make the necessary deduction for impurities in the sal soda and zinc oxide. Divide the number of cubic centimeters permanganate taken by ten. *Deduct 0.02 per cent.*

Following are some comparisons of results by this method with results by Volhard's method, gravimetric method, and color method:

TABLE XI.

No.	Volhard with all precautions. Per cent.	Stone with all precautions. Per cent.	Gravimetric. Per cent.	Color. Per cent.
1451	0.51	0.51	0.52	0.53
452	0.44	0.42	0.43	0.435
453	0.46	{ 0.42 / 0.43	....	0.425
453	0.47	0.45	0.46	0.45
493	0.46	0.47	....	0.46
466	0.41	0.41	0.41	0.43
466	0.49	0.49	0.485	0.49
481	0.45	0.46	0.455	0.469
153	0.64	0.65	....	0.64

A SIMPLE FORM OF GAS REGULATOR.[1]

BY LUDWIG SAARBACH.

Received April 17, 1896.

A GLASS tube, one end of which is blown out to a bulb is bent around twice, as indicated in Fig. 1, and is provided with a side tube *T*. Some mercury is poured into it, which cuts off a volume of air in bulb *A*. The smaller tube *I* fitting loosely in the wider tube, is connected with the latter by a piece of rubber tubing, which at the same time allows an up and down

[1] Read before the New York Section, April 10th, 1896.

movement of the small tube. This apparatus is put into the air or water bath, which is to be kept at a constant temperature; its working is effected by the expansion by heat of the

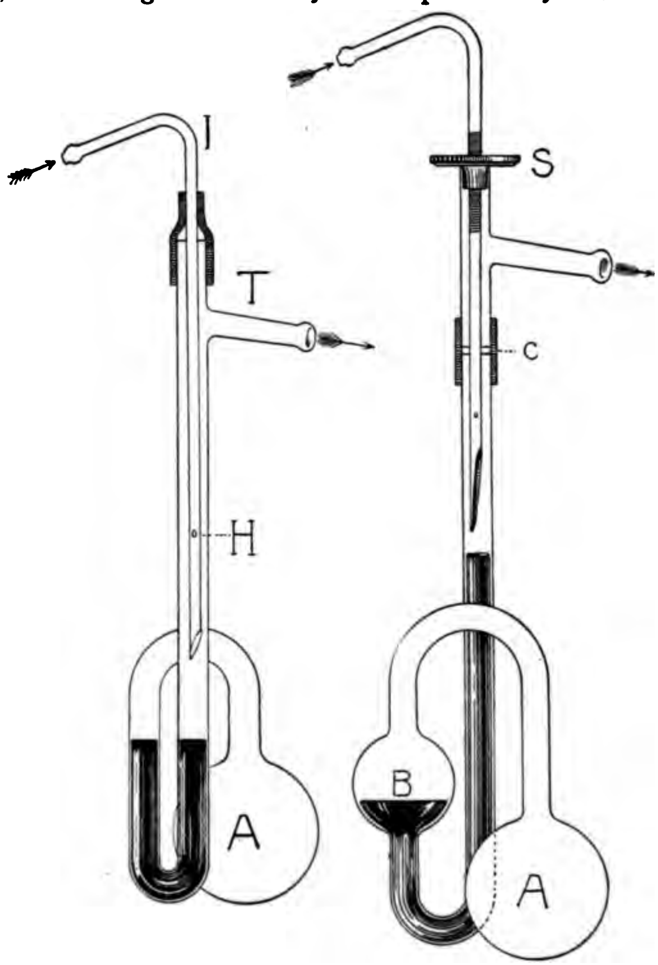


Fig. 1. Fig 2.

volume of air in bulb A, which causes the mercury column to rise until it reaches pipe I, serving as inlet of the gas. From the space over the mercury column, the gas is conducted through the pipe T to the burner. As the inlet pipe is cut off

obliquely or drawn out to a slit, the supply of gas is with increased temperature diminished by and by, and might even be cut off altogether if the pipe were not provided with a small hole *H*, which allows the passage of a sufficient amount of gas to prevent the extinction of the flame. The smaller supply of gas lowers the temperature, and the sinking of the column of mercury caused thereby allows then the gas to pass again freely. It is easy to keep the air- or water-bath, which is provided with this apparatus, constantly at any desired temperature within 1° to 2° F. by regulating the position of the inlet pipe. The daily changes in the atmospheric pressure have very slight influence.

As the amount of mercury might at higher temperature not be sufficient to keep back the expanded air a small bulb might be blown in the second bend (B, Fig. 2), and thereby a sufficient supply of mercury for even very high temperatures can be provided. If the apparatus is intended for a closed bath, the main pipe is cut at *C*, the lower part is then fixed from inside and connected outside with the upper part by means of rubber tube. The standpipe *I* may also be regulated by a screw movement *S*.

This apparatus has the advantage of being simple and cheap. It can be used for open or closed baths at either high or low temperatures. The main drawback of all other similar apparatus is the black mass caused by the action of illuminating gas on the mercury, which collects in a short while on the surface of the mercury column and stops the action completely. The apparatus described allows the removal of the dirty mercury and filling anew in the easiest and most rapid manner.

Furthermore, there is no stop-cock or rubber tube connection between the working parts, that is, the expanded volume of air and the column of mercury.

A RAPID METHOD OF DETERMINING THE MOLECULAR MASSES OF LIQUIDS BY MEANS OF THEIR SURFACE TENSIONS.

BY C. E LINEBARGER.

Received May 13, 1896.

INTRODUCTORY.

UNTIL within the last few years our knowledge of the molecular condition of liquids was very limited. Such facts as the existence of allotropic modifications of elements and of isomorphous forms of compounds, the rotation of the plane of polarized light, the abnormal vapor-densities of certain substances in the vicinities of their boiling points seemed to indicate that in liquids two or more gaseous molecules coalesce to form complex molecular groupings.[1] Indeed, de Heen[2] developed a theory of liquids on the hypothesis that liquid molecules are made up of a number of gaseous molecules, thus making a distinction between "liquidogenic" and "gasogenic" molecules. On the other hand, it has been assumed by some that the differences between gases and liquids are due solely to the greater propinquity of the molecules in the liquid condition, no polymerization of the gaseous molecules taking place. But nothing really definite about the question was advanced until Guye,[3] in studying the relation of his critical coefficient to the molecular mass of a liquid at its critical point, found that it was necessary to double the molecular masses of methyl alcohol and water in order to make them conform to the general rule he had established. This is the first time that a definite numerical value was assigned to the molecular mass of a liquid, and it was thereby rendered evident that both of the above suppositions in regard to the molecular condition of liquids correspond to fact; some liquids are polymerized and some are not.

1 Naumann: *Ann. Chem.* (*Liebig*), 155, 325, *1870*; Henry: *Ann. de la Soc. Scientifique de Bruxelles*, *1878-1879*, 267; Spring: *Bull. del'Acad. de Belgique* [3], 11, No. 5, *1886*; Dupré: Théorie mécanique de la chaleur, 147; Amagat: *Ann. chim. phys.* [5], 11, 536; Ramsay: *Proc. Roy. Soc.*, *1880*, April 22 and December 16; Ramsay and Young: *Proc. Roy. Soc.*, *1885*, Nov. 19, and *Phil. Mag.*, *1887*, 129.

2 de Heen: *Ann. chim. phys.* [6], 5, May, *1885*, and Physique Comparée et la Theorie de Liquides, *1888*.

3 *Ann. chim. phys.* [6], 21, Oct. *1890*; *Compt. rend.*, 110, 141 and 1128, *1890*; *Bull. Soc. Chim.* [3], 3, 51; Arch. de Genène. [3], 23, 197; Thesis: Le coefficient critique et la determination du poids moleculaire au point critique. Paris, *1891*.

The next stage in the investigation of the subject was naturally the determination of the classes of liquids that are made up of simple molecules and of the classes of liquids that consist of complex molecules, or, in other words, the determination of which liquids are "normal" and which are "associated;" also the question as to the amount of association presented itself.

This investigation was taken up by Ramsay and Shields,[1] who, by the application of a method based upon determinations of surface energies, examined more than fifty liquids; this work may justly be considered classic and is the source of most of our definite knowledge of the size of liquid molecules.

The division of liquids into two classes according to their molecular polymerization having thus been rendered familiar and definite by the work of these two English chemists, many properties of liquids were subjected to examination in order to ascertain whether they might reveal any indications of molecular polymerization. Guye[2] has been particularly active in this direction; thus, he found evidence of molecular association in certain liquids, as shown by their latent heats of vaporization attaining a maximum, their curves of vapor-tensions intersecting one another, etc. Also, Linebarger,[3] in examining Pictet's Law (commonly but erroneously known as Trouton's Law) and in determining the specific gravities, viscosities, and other physical properties of mixtures of liquids found that certain abnormalities could be best accounted for by the assumption of the presence of polymerized molecules. Moreover, in studying the vapor-tensions of mixtures of volatile liquids, Linebarger[4] was led to the discovery of a method of determining the absolute molecular mass of a liquid at a definite temperature, Ramsay and Shield's method giving only the average molecular mass throughout a certain range of temperature.

Mention must also be made of an extremely simple method proposed by Traube[5] for ascertaining whether the molecules of a liquid are in a state of association or not; it is based upon a

[1] *J. Chem. Soc.*, 63, 1089, *1893*, and *Ztschr. phys. chem.*, 12, 433, *1893*.
[2] Arch. de Genève [3], Jan., Feb., and May, *1895*; *Bull. Soc. Chim.*, 13, 34, *1895*.
[3] *Am. J. Sci.*, 49, 381, *1895*; *Am. Chem. J.*, 18, 429.
[4] *J. Am. Chem. Soc.*, 17, 615 and 690, *1895*.
[5] *Ber. d. chem. Ges.*, *1894–1896*.

determination of the density of the liquid under investigation.

The discovery of a method of determining the molecular masses of liquids opens up a broad field of investigation. The discoverer of a new liquid ought no longer to be content with a determination of its vapor-density or cryoscopic behavior in order to ascertain its molecular mass in the gaseous or dissolved state; he ought also to determine its surface tension, its density, or its vapor-tension in solution in order to ascertain whether it is associated or not. The method of vapor-tensions in solution, although it is the only one as yet devised that gives indications of the exact size of a liquid molecule at a given temperature, is rather long and is restricted to volatile liquids capable of analysis in the presence of the solvent. The chemist is therefore confined to the methods by Ramsay and Shields, or Traube. As stated above, Traube's method depends simply upon a determination of density; it does not seem to have attracted much attention, probably because it has merely an empirical basis. But a density determination is also required in Ramsay and Shields' method, so that the two methods may be employed together, the one serving as a control of the other.

The method of determination of molecular masses of liquids from their surface energies, as carried out with the apparatus used by Ramsay and Shields, does not seem to have been generally introduced into laboratories of organic chemistry for the probable reason that it requires careful and skillful manipulation and considerable time. There appears to be a need for an apparatus that can be handled rapidly, does not require much skill in using, is always ready for work, and gives reliable results. It is believed that the apparatus to be described in the following sections meets these requirements.

II. DESCRIPTION OF APPARATUS.

The apparatus (Fig. 1) consists of the following pieces: A column of brass tubing *AA* with iron tripod base; a short horizontal arm *B*, to which is attached a brass gibbed plate *SS* supporting the capillary tubes by means of the clamps *CC* and *DD*, and also the micrometer screw *EF*; a retort ring *AH* bearing the beaker *II*; a compression device consisting of a screw *L*

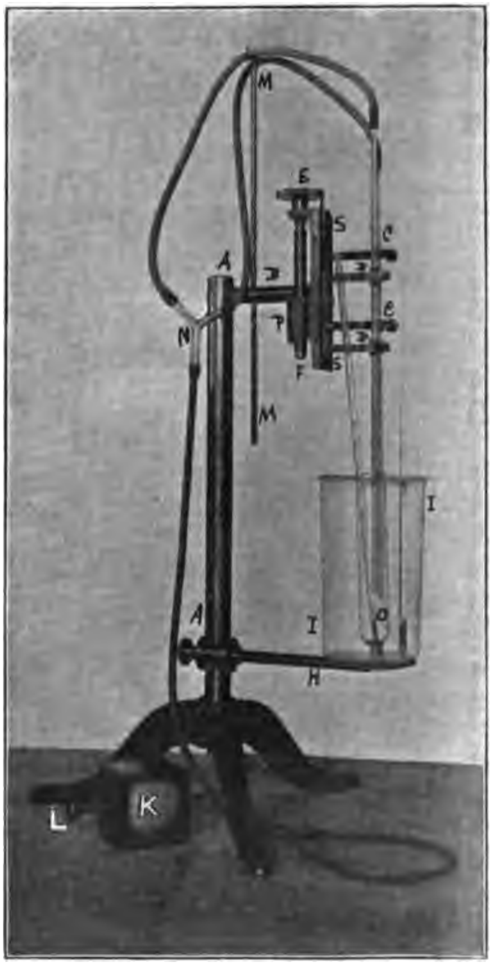


Fig. 1. Apparatus for Determining the Surface Tensions of Liquids. (*To Face p. 516.*)

pressing into a rubber ball *K*, which is connected by means of rubber tubing and a glass Y tube *N* to the upper extremities of the capillary tubes; a vertical rod *MM* passing through the arm *B* (to which it may be clamped by a thumb-screw not shown in the figure) and provided with rings to support the rubber tubes connected with the capillary tubes, the latter being thus relieved of the weight of the former; a test tube *O*, into which the capillary tubes pass, supported by the cover of the beaker *H*; two thermometers, one to take the temperature of the bath-liquid contained in the beaker, the other that of the liquid undergoing investigation in the test tube *O*.

Some of these pieces require a more detailed description.

The immovable part of the gibbed plate has a scale fastened along its side divided into fortieths of an inch, while its movable part has a pointer playing over this scale. Back of the gibbed plate is fixed the bearing *P*, in which the screw *EF* turns; the clamps *CC* are attached to the fixed portion of the gibbed plate, also another pointer for the milled head of the screw.

The micrometer screw demands a specially detailed description, inasmuch as the accuracy of the results obtainable by the apparatus depend mainly upon the accuracy of its construction. The one I use has forty threads to the inch, is about four inches long, and of good diameter, so as to give absolute motion, the adjustable split bearing *P* taking up all lost motion. Great pains were taken in turning it, and I have been unable to detect any irregularities in its construction; indeed, the screw furnished by the makers is even more accurate than is really necessary. The milled head *E* (about thirty-five mm. in diameter) is divided into 100 parts, thus giving a direct reading of $\frac{1}{4000}$ of an inch, and even less than that, since it is easy to estimate fractions of a division.

Three capillary tubes were employed in working with the apparatus:

A with a bore of about one and a half mm.
B " " " " " five-tenths mm.
C " " " " " one-tenth mm.

From the nature of the method it is not at all necessary to know the exact dimensions of the tubes; all that is required is

that the bore be approximately circular and the edges sharp. To prepare the capillary tubes, a stock of tubing is examined and tubes of the desired dimensions selected. Pieces are broken off from these tubes until it is found that the ends present plane surfaces perpendicular to the axis of the tube. If the clamps happen to be too large for the tubes, a filling of sheet lead may be employed.

The liquid serving as bath and contained in the beaker may be water or glycerin; it is heated by means of a Bunsen burner and kept in motion by means of a stirrer (not shown, however, in the figure). Besides this kind of a bath much use was made of a vapor jacket for keeping the temperature uniform during a determination. The test tube *O* was fitted into a considerably larger tube by means of a cork, through a second perforation of which passed a long glass tube acting as a condenser. On boiling liquids or mixtures of liquids in the larger tube, their vapors rise and heat the inner tube with its contents to a desired constant temperature for any length of time.

III.—METHOD OF MAKING A DETERMINATION.

The first thing to do in using the apparatus is to get the lower extremities of the two capillary tubes at the same level. This may be accomplished in the following simple manner. A spirit-level is placed upon a piece of plate glass, which in turn is set upon the support *H* at the required height and levelled. The pointers of the side scale, as well as that of the screw head, are set at zero, the tubes allowed to rest freely upon the plate glass, and then clamped into position. While this way of fixing the tubes answers well enough for the initial adjustment of the apparatus, it is not sufficiently accurate to insure their being replaced in the same position, if, from any cause, they become displaced. Indeed, it is not at all certain that the tubes are at the same level to within 0.1 mm., when adjusted in the above manner; yet this degree of accuracy is entirely sufficient for the first adjustment, and later it will be shown how they can be gotten into the same position to within 0.01 mm.

The test tube has a mark scratched on its side, which indicates the volume of liquid that is to be taken for a determination

of its capillary constant, it having been found that differences in the distance between the surface of the liquid and the orifices of the tubes have a little influence upon the readings of the instrument.[1] The volume of the liquid may be as small as a couple of cubic centimeters, if a small test tube be used; generally, however, it is advisable to employ from five to ten cc. The test tube is filled with the liquid under examination to this mark and the tube suspended in the bath. The beaker is placed upon a piece of asbestos board or wire gauze set upon the retort ring, which is raised until the capillary tubes are close to the bottom of the test tube. A thermometer is introduced into the liquid, and the bath liquid stirred so as to insure uniformity of temperature.[2] The rapidity with which the liquid undergoing investigation takes on the temperature of the bath may be hastened by blowing bubbles up through it by compression of the air in the rubber ball *K*.

When the temperature of the liquid is the same as that of the bath, the movable tube (preferably the one with the smaller bore), is raised by turning the screw. This may be done rapidly while bubbles are being forced out of the larger tubes every second or so. At a certain point bubbles may cease to issue from the larger tube and commence to come from the smaller one, an indication that the correct adjustment has been passed. The screw is now turned very cautiously in the opposite direction until bubbles issue at about the same time from both of the tubes. The final adjustment is generally best made as follows:

The air is compressed *very slowly* until it has arrived just at the orifices of both tubes. The pressure is then not increased further, and, as a rule, it will be observed that, if the adjustment is perfect, bubbles will issue of their own accord from both the tubes in a second or so; sometimes one of the bubbles lags a little behind the other. The success of the operation depends upon the *steady* and *gradual* compression of the air; if this be subjected to abrupt or irregular changes of pressure, not inconsiderable errors may be committed. It is advisable to make at

[1] This influence is, however, but slight. Readings with ether were found to differ by only $\frac{1}{200}$ of an inch, when the difference between the free surface of the liquid and the lower extremities of the capillary tubes differed by more than four inches.

[2] The mode of procedure is essentially the same when a vapor jacket is employed.

least two readings, one when the narrower tube is being lowered, the other when it is being raised; indeed, the readings can be made so rapidly that it is a good plan to take a half dozen or so, the tubes being moved alternately up and down.

IV.—DISCUSSION OF SOURCES OF ERROR IN APPARATUS.

In the determination of the capillary constants by means of the apparatus described in the preceding sections, measurements of three kinds have to be made, *viz.*, measurements of specific gravity, of temperature, and of the distance between the lower extremities of the capillary tubes. We pass to the discussion of the errors inherent to each.

I. The determination of the surface tensions by any of the direct methods, such as measuring the height to which liquids rise in capillary tubes, etc., cannot be said on an average to be accurate to more than one part in two thousand, and only in exceptional cases to one part in ten thousand. On the other hand the accuracy of a specific gravity determination can easily attain one part in ten thousand, and in many cases to even one part in a hundred thousand. In the formula to be communicated in the following section, it will be seen that the influence of the specific gravity upon the value of the capillary constant is not very great, so that a determination of the specific gravity to one part in two thousand is perhaps sufficiently accurate for our purposes, although it is of course better to be sure of the fourth decimal place. We may conclude then that the accuracy of a determination of the specific gravity of a liquid where surface tension is to be ascertained, may be counted perfect, if it be made to within one part in ten thousand.

II. For temperatures between 0° and 50° it is an easy matter to keep the temperature of even such a simple bath as the one given in Fig. 1 constant to within 0.05° long enough to adjust the apparatus and make several readings. By the use of the larger baths, or, better still, of vapor jackets, the temperature can be kept sufficiently uniform for the investigation at different temperatures of most liquids. As a variation of temperature amounting to 0.1° changes but little the readings of the apparatus, it may be allowed that the error committed in estimating the temperature is, for the purpose of this investigation, negligible.

III. The possible error that may be committed in the readings of the apparatus can best be judged by considering the readings themselves. A number of series of readings for different liquids at various temperatures are accordingly given just as they were taken directly from the apparatus.

The readings are not to be taken as material for the calculation of the surface tensions of the liquids, as in some cases they do not represent the true distances between the lower extremities of the capillary tubes, the positions of these having been altered purposely several times. The unit of a reading is a fortieth of an inch.

Nitroethane[1] at 16.95°. Tubes A and B.

23.27
23.26
23.28

Nitroethane[1] at 46.6°. Tubes A and B.

21.23
21.26
21.21

Nitromethane[1] at 24.5°. Tubes A and B.

24.28
24.26
24.23
24.25
24.29
24.26
24.26

Nitromethane[1] at 41.5°. Tubes A and B.

22.86
22.87
22.80
22.81
22.85

Benzene at 20.0°. Tubes A and B.

22.86
22.88
22.85
22.86
22.87

Benzene at 20.5°. Tubes B and C.

30.55
30.54
30.59
30.56
30.55

Toluene at 25.0°. Tubes A and B.

24.42
24.44
24.41
24.40
24.43

Another series made ten days later.

24.43
24.45
24.42
24.43
24.45

Toluene at 46.6°. Tubes A and B.

22.65
22.63
22.62
22.63
22.64
22.64
22.66
22.64

[1] Made by Mr. L. W. Jones, of the University of Chicago.

Methyl nitrate at 0.2°. Tubes A and B.	Carbon bisulphide at 19.5°. Tubes A and B.
18.29	19.35
18.28	19.32
18.25	19.30
18.26	19.33
18.28	19.34

Ethyl ether at 0.1°. Tubes A and B.	Ethyl ether at 25.0°. Tubes A and B.
17.90	13.55
17.92	13.53
17.92	13.52
17.95	13.54
17.93	Another series made over a month later.
	13.54
	13.55
	13.53

Toluene at 78.4°. Tubes B and C.	Monochlorbenzene at 77.8°. Tubes B and C
24.73	23.34
24.77	23.38
24.75	23.32
24.71	23.35
24.74	23.34

Ethyl iodide at 25.0°. Tubes A and B.	Ethyl alcohol at 51.0°. Tubes A and B.
8.89	18.65
8.87	18.62
8.88	18.64
8.88	18.61
8.87	18.63
Another series made twenty days later.	
8.87	
8.86	
8.88	

Water at 40.0°. Tubes A and B.	Water at 20.0°. Tubes A and B.
77.10	76.09
77.13	76.13
77.14	76.10
77.09	76.16
77.11	76.23
77.16	76.14
77.13	76.16
77.12	76.18
	76.15
	Another series made a fortnight later.
	76.12
	76.18
	76.21
	76.19
	76.14
	76.18

These series of numbers have been taken from my note books almost at random, and are but a small portion of the number of readings I have made. They show that for most liquids differences in the readings amounting to more than $\frac{5}{4000}$ of an inch seldom occur, and when a series of readings are made and their average taken, the error almost vanishes. Only in case of water were greater differences of readings observed; yet, since water has such a large capillary constant, the error committed is very slight. It was observed that the nearer the extremities of the capillary tubes were, and, consequently, the smaller the numerical value of the reading, the more concordant were the readings.

While the three sources of error just discussed seem to be almost negligible, there is another, inherent, not in the apparatus, but in the method, which stands seriously in the way of obtaining reliable absolute determinations of the surface tensions of liquids. This source of error lies in the determination of the "apparatus constant," which may vary from one liquid to another. A more detailed discussion of it will be given in the next section, after the way in which the "apparatus constant" is determined is described.

V.—CALCULATION OF RESULTS.

Having now shown the degree of accuracy attainable in the readings of the apparatus under discussion, I will pass to the consideration of the manner in which the results obtained by this indirect method may be converted into those arrived at by direct methods. As stated above, two things besides the temperature are measured in this method: (1) the specific gravity of the liquids taken, and (2) the vertical distance between the lower ends of the two capillary tubes when air under the same pressure issues in synchronous bubbles from their orifices. It is not difficult to determine the specific gravity to within $\frac{1}{50000}$, although an accuracy of $\frac{1}{10000}$ is quite sufficient. The distance between the ends of the two tubes can be measured to about a hundredth of a millimeter, except in the case of water, where the degree of accuracy of measurement is only within a tenths of the same unit of length. It is now our task to pass from the data obtained from measurements of these quantities to the capillary constants measured in dynes per centimeter.

Inasmuch as our knowledge of the form of the bubbles just on the point of issuing from the orifices of the capillary tubes is not at all precise, there appears to be no immediate way of finding a relation on theoretical grounds between the data furnished by this indirect method and those given by direct methods. Jäger[1] obtained the relationship employed by him in the following manner: "Wie sich unsere Annahme für die Formulirung des Einflusses, welchen die Röhrenweite auf den bewussten capillaren Druck hat, als richtig erwies, so zeigt sich, wie wir später sehen werden, dass es vollständig genügt, wenn wir

$$\alpha F(s) = \alpha(1 + \beta s)^{2}$$

setzen, wobei β eine Constante bedeutet, die sich ebenfalls leicht ermitteln lässt, wenn zwei Flüssigkeiten, deren α und s bekannt sind, zu Gebote stehen. Verwenden wir nämlich zu unseren Messungen stets dieselben beiden Capillarröhren, so wird für die eine Flüssigkeit die Gleichung (1)

$$\alpha(1 + \beta s)\varphi(r.r') = hs,$$

für die zweite,

$$\alpha'(1 + \beta s')\varphi(r,r') = h's',$$

somit

$$\frac{\alpha(1 + \beta s)}{\alpha'(1 + \beta s')} = \frac{hs}{h's'}.$$

Aus dieser Gleichung kann der Werth von β ermittelt werden da alle übrigen in ihr vorkommenden Grössen bekannt sind."

In order to obtain the value of β, he made use of Brauner's[3] and Wolf's[4] directly determined data for water and ethyl ether. By transforming the immediately preceding equation into

$$\alpha = \frac{\alpha' hs(1 + \beta s')}{h's'(1 + \beta s)},$$

he obtained therefrom on putting

$$\frac{\alpha'(1 + \beta s')}{h's'} = c,$$

$$\alpha = c\frac{hs}{1 + \beta s};$$

[1] *Loc. cit.*
[2] a = capillary constant; s = specific gravity.
[3] *Ann. der Phys. Pogg.*, 70, 515.
[4] *Ann. der Phys. Pogg.*, 70, 575.

and substituting for specific gravity $= s$, the specific volume $=$ $v = \frac{1}{s}$, he finally obtained

$$\alpha = c\,\frac{h}{v+\beta},$$

an equation used throughout his work in transforming his results.

It is hardly necessary to mention that the degree of accuracy that can be attributed to an indirect method of measuring a physical constant of Nature depends upon the accuracy of the results obtained by direct methods; hence the importance of choosing the most exact directly determined data for the calibration of an indirect method. Ramsay and Shields[1] have elaborated the method of measuring the heights to which liquids rise in capillary tubes, and have carried out series of determinations of the capillary constants of various liquids in contact only with their own vapor and glass, which are justly regarded as of the greatest trustworthiness, and may be confidently taken as standards.

If Jägers equation,

$$\frac{\alpha(1+\beta s)}{\alpha'(1+\beta s')} = \frac{hs}{h's'},$$

be correct, it ought to be possible to obtain the same value of β, when the data for α and α', s and s', and h and h' are taken for any pair of liquids. On carrying out the calculations, however, I found, on employing the data given by Ramsay and Shields,[2] for the specific gravities and capillary constants, and the readings of my apparatus for the differences of level between the extremities of the two capillary tubes, that the values of β varied considerably for different pairs of liquids. Furthermore, it was found that, if β and c be calculated for any two liquids, and then from the equation

$$\alpha = c\,\frac{hs}{1+\beta s},$$

the value of α be deduced for a third liquid, differences between the values thus obtained and those given by Ramsay and Shields amounting to five or ten per cent. were obtained in some cases,

[1] *Ztschr. phys. Chem.*, 12, 433, 1893.
[2] *Loc. cit.*

although once in a while a pretty good correspondence was observed. Jäger's equation appears to be merely approximate and does not stand a rigid scrutiny. Jäger himself seems to find the justification of his formula in its yielding results corroborative of certain theoretical views he advances, and in the agreement between his observed values and those calculated for the same temperatures, by means of temperature coefficients; but as the temperature coefficients were derived from his own data, which differ but rarely more than five or ten per cent. from those communicated by Ramsay and Shields,[1] and he does not attain to a much closer correspondence than that between his observed and calculated values, the correctness of the formula does not seem to be any the better established.

It accordingly became peremptory to devise another formula which should be in better accordance with Ramsay and Shields'[2] measurements. But here a difficulty arose. Ramsay and Shields determined the capillary constants of liquids that had been freed from air; the liquids were in contact only with their own vapor and glass. There is no doubt but that the surface tensions of liquids can be measured accurately by means of their rise in capillary tubes only when no air is present; R. Schiff[3] had already made this observation before Ramsay and Shields. Just what influence the presence of air has upon the capillarity of liquids we do not know; the greater or less volatility of a liquid makes the degree of dilution of air in contact with its surface correspondingly greater or less. In the apparatus described in this article, the liquid under examination is saturated with air, and the pressure of the air varies with the specific gravity of the liquid. The difficulty at issue lies in the question as to whether the indirect determinations made with liquids in contact with air are comparable to more than a gross approximation with those obtained by the direct method as employed by Ramsay and Shields. This difficulty seemed at first to be unsurmountable, but, finally, a simple relation was discovered which shows an excellent correspondence between Ramsay and Shields' data and mine.

1 *Loc. cit.*
2 *Loc. cit.*
3 Ann. Chem. (Liebig), 233, 47.

The relation in question is

$$\gamma = chs + s^2 \ldots\ldots\ldots (A)$$

wherein γ represents the capillary constant in dynes per centimeter, c the "apparatus constant," h the distance between the ends of the tubes, and s the specific gravity. The value of the constant was obtained in the following way. The data for γ and s were taken from Ramsay and Shields' and Ramsay and Aston's papers, and those for h from my own measurements. These were set in equation (A) and the value of c calculated therefrom. The greatest pains were taken in the purification of the liquids examined, so that they had no doubt the same properties as those used by the investigators just named. The data and results of the calculations are given in Table I. for the tubes A and B, and in Table II. for tubes B and C.

TABLE I.

Values of "Apparatus Constant" for Tubes A and B.

Name of liquids.	T.	s.	γ.	h.	c.
Water	20.0°	0.9984	70.72	55.60	1.248
"	30.0°	0.9958	69.10	54.85	1.247
"	40.0°	0.9923	67.50	53.90	1.245
Methyl alcohol ...	20.0°	0.7905	23.03	23.16	1.227
Ethyl " ...	20.0°	0.7900	22.03	21.97	1.236
Acetone	16.8°	0.7798	23.35	22.95	1.238
"	46.4°	0.7656	19.68	20.00	1.250
Ethyl ether	20.0°	0.7143	16.49	17.91	1.245
" "	30.0°	0.7000	15.27	16.87	1.252
Ethyl iodide	19.1°	1.937	30.00	10.88	1.248
Carbon bisulphide	9.7°	1.2773	32.73	19.90	1.224
Benzene	11.2°	0.8871	29.21	25.86	1.239
"	46.0°	0.8500	24.71	22.75	1.241
Chlorbenzene	9.5°	1.1182	33.71	23.46	1.238
"	45.6°	1.0795	29.30	21.25	1.227
Toluene	15.2°	0.8682	28.18	25.21	1.253
"	46.6°	0.8380	24.60	22.65	1.259
				Average =	1.243

TABLE II.

Values of "Apparatus Constant" for Tubes B and C.

Names of liquids.	T.	s.	γ.	h.	c.
Acetone	16.8°	0.7998	23.25	27.72	1.023
"	46.4°	0.7656	19.68	24.22	1.029
Chlorbenzene.....	45.6°	1.0795	29.30	25.71	1.014
"	77.8°	1.0444	24.65	23.38	1.011
Ethyl ether	20.0°	0.7143	16.49	22.08	1.036
Benzene	11.2°	0.8871	29.21	31.44	1.019
"	46.0°	0.8500	24.71	27.86	1.013
Toluene	15.2°	0.8682	28.18	30.60	1.032
"	46.6°	0.8380	24.60	27.75	1.028
"	78.4°	0.8080	20.93	24.75	1.014
				Average =	1.022

A glance at the tables shows that the "constants" are indeed quite constant. In Table I., the average of the numbers in the last column is 1.243; the greatest variation on one side is 0.019 for carbon bisulphide at 9.7°, and on the other side, 0.016 for toluene at 46.6°. Generally, the differences from one liquid to another are not larger than they are for the same liquid from one temperature to another. Likewise, in Table II., the average value of the constant is 1.022, with differences of 0.014 for ether at 20.0° on the one hand, and 0.011 for chlorbenzene on the other.

Introducing $c = 1.243$ from Table I. and $c = 1.022$ from Table II. into equation (A), and treating α as the unknown quantity, I calculated the capillary constants to be those given in Tables III. and IV., respectively, beside which are placed the corresponding data given by Ramsay and Shields[1] and Ramsay and Ashton.

TABLE III.

Comparison of Capillary Constants for Tubes A and B. $c = 1.234$.

Names of liquids.	Temp.	γ. $\gamma = chs. + s^2$.	γ. Ramsay & Shields.	$\gamma - \gamma$.
Water...............	30.0°	68.82	69.10	—0.28
"	40.0°	67.42	67.50	—0.08
Methyl alcohol......	20.0°	23.39	23.03	+0.36
Ethyl alcohol	20.0°	22.17	22.03	+0.14

[1] *Loc. cit.*

Names of liquids.	Temp.	γ. $\gamma = chs. + s^2$.	γ. Ramsay & Shields.	$\gamma - \gamma$.
Acetone	16.8°	23.34	23.35	—0.01
"	46.4°	19.59	19.68	—0.09
Ethyl ether	20.0°	16.42	16.49	—0.07
" "	30.0°	15.18	15.27	—0.09
Ethyl iodide	19.1°	29.90	30.00	—0.10
Carbon bisulphide	9.7°	32.22	32.73	—0.49
Benzene	11.2°	29.31	29.21	+0.10
"	46.0°	24.75	24.21	+0.04
Chlorbenzene	9.5°	33.86	33.71	+0.15
"	45.6°	29.68	29.30	+0.38
Toluene	15.2°	27.96	28.18	—0.22
"	46.6°	24.25	24.60	—0.35

TABLE IV.

Comparison of Capillary Constants for Tubes B and C. $c = 1.022$.

Names of liquids.	T.	γ. $\gamma = chs + s^2$	γ'. Ramsay & Shields.	$\gamma - \gamma'$.
Acetone	16.8°	23.32	23.35	—0.03
"	46.4°	19.64	19.68	—0.04
Chlorbenzene	45.6°	29.56	29.30	+0.26
"	77.8°	26.01	25.66	+0.35
Ethyl ether	20.0°	16.42	16.49	—0.07
Benzene	11.2°	29.28	29.21	+0.07
"	46.0°	24.88	24.71	+0.11
Toluene	15.2°	27.93	28.18	—0.25
"	46.6°	24.46	24.60	—0.14
"	78.4°	21.09	20.93	+0.16

It is at once apparent that only in a few instances the differences between Ramsay and Shields' results and mine amount to more than a few tenths of a per cent., and in some cases the correspondence is as good as perfect. Furthermore, the differences that are found seem to be very nearly the same when either pair of tubes is employed ; this indicates that the differences are due rather to the possible differing degrees of purity in the liquids employed by each of us than to a fault in the apparatus itself. However that may be, the data show that it is possible to obtain with the apparatus in question results, which by means of the formula (A), are comparable with those obtained by Ramsay and Shields or Aston. One cannot withstand the temptation to quote Jäger's words :[1] "........unsere

[1] *Loc. cit.*

methode is vollständig geeignet, richtige Resultate zuergeben. Fasst man noch die leichte, sichere und wenig zeit beanspruchende Handhabung, welche unser Apparat erfordert, ins Auge, so wird man wohl leicht zur Ueberzeugung gelangen, dass unter den gegenwärtigen Methoden für den praktischen Gebrauch kaum eine bessere zu finden sein dürfte." As to what pertains to the experimental handling of the apparatus, my experience with it enables me to subscribe to the above. But a restriction has to be made in regard to the conversion of the indirect results into direct ones. Jäger's formula has been shown above to be only approximately correct, and the one I propose has but an empirical basis. Although it has been found to stand the test of comparison with ten liquids of different properties, when two sets of tubes were employed, it is not allowable to claim that it will furnish reliable results for any liquid whatsoever. In other words, the instrument cannot be depended upon to give absolute data, since the "apparatus constant" may differ from liquid to liquid. Still it is not at all probable that the variations in the value of the "apparatus constant" will be very great in any case, and, as a variation of as much as ten per cent. has but a relatively small influence upon the surface tension, the method may be considered to give results accurate enough for the calculation of molecular masses, since Ramsay and Shields do not claim for their method an accuracy of more than six or seven per cent.

VI. MODE OF PROCEDURE IN DETERMINING THE MOLECULAR MASSES OF LIQUIDS.

In determining the molecular mass of a liquid it is well to measure its surface-tension at three different temperatures, and for this purpose vapor jackets will be found convenient. Temperatures easy to get are (1) that of the atmosphere 10° to 25°; (2) that of boiling carbon bisulphide, about 46°; (3) that of boiling alcohol, about 78°. Of course, other liquids than these may be used, all that is required is that the temperatures obtained are 20°–30° apart.

The liquid is placed in the test tube *O*, and carbon bisulphide is poured into the jacketing tube. The capillary tubes are im-

mersed in the liquid, and, after the temperature has become uniform, several readings are made, their average being taken. The carbon bisulphide is now boiled and when the temperature has become constant a second series of readings is made. The flame is removed and, after the liquid has cooled down a little, alcohol is substituted for the carbon bisulphide. The alcohol is now boiled and a third series of readings taken when the temperature becomes stationary. All of these operations can be easily made in less than an hour.

It is possible to determine the specific gravity of the liquid at the different temperatures during the above operation, as the capillary apparatus requires but little continuous attention, most of the time taken up in a determination being needed in warming the liquid to a constant temperature. Any of the ordinary methods of density determinations may be employed which can give it to the third or fourth decimal place.

The necessary calculations may be illustrated by a couple of examples, one of a normal liquid, the other of an associated liquid. For the theoretical grounding and fuller explanation of the method, reference must be had to Ramsay and Shields' paper.[1]

BENZENE.

$$\gamma = chs + s^2 = (1.243 \times 25.86 \times 0.8871) + 0.80 = 29.31 \text{ dynes at } 11.2^\circ.$$

$$= (1.243 \times 22.75 \times 0.85) + 0.72 = 24.75 \text{ dynes at } 46.0^\circ.$$

$$\gamma(Mv)^{\frac{2}{3}} = (78/0.8871)^{\frac{2}{3}} \times 29.31 = 575.1 \text{ ergs at } 11.2^\circ.$$

$$(78/0.8500)^{\frac{2}{3}} \times 24.75 = 501.8 \text{ `` `` } 46.0^\circ.$$

$$\frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = \frac{575.1 - 501.8}{46.0 - 11.2} = \frac{73.3}{34.8} = 2.106.$$

The value assigned to the constant by Ramsay and Shields is 2.121, from which the constant just calculated differs by only 0.015; hence benzene is a normal liquid.

[1] *Loc. cit.*

ACETONE.

$$\gamma = chs + s^2 = (1.022 \times 27.75 \times 0.7998) + 0.64 = 23.32 \text{ dynes at } 16.8^\circ.$$

$$(1.022 \times 24.22 \times 0.7656) + 0.59 = 19.55 \text{ dynes at } 46.4^\circ.$$

$$\gamma(Mv)^{\frac{2}{3}} = (58/0.7998)^{\frac{2}{3}} \times 23.32 = 406.1 \text{ ergs at } 16.8^\circ.$$

$$(58/0.7656)^{\frac{2}{3}} \times 19.55 = 351.6 \text{ `` `` } 46.4^\circ.$$

$$\frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = \frac{406.1 - 351.6}{46.4 - 16.8} = \frac{44.5}{29.6} = 1.840.$$

The smallness of this constant indicates association in acetone. To determine the amount of association, we multiply the molecular mass M, by a factor x, which represents the average number of simple molecules that have coalesced to form a complex molecule. The calculation is as follows:

$$\left(\frac{2.121}{1.840}\right)^{\frac{3}{2}} = 1.25 \text{ between } 16.8^\circ \text{ and } 46.4^\circ.$$

the average molecular mass throughout this range of temperature is accordingly $1.25 \times 58 = 73$.

The apparatus described above was made by Walmsly, Fuller & Co., of Chicago, and has proven satisfactory in every detail. The makers inform me that they are ready to furnish the apparatus provided with a micrometer screw divided according to the metric as well as the English system.

ON THE REACTION BETWEEN CARBON TETRACHLORIDE AND THE OXIDES OF NIOBIUM AND TANTALUM.

BY M. DELAFONTAINE AND C. E. LINEBARGER.

Received April 20, 1896.

EUG. DEMARCAY[1] states that if the vapor of carbon tetrachloride be passed over the oxide of niobium or of tantalum heated below redness, the metallic oxides are converted into chlorides. "Dans le cas de l'acide niobique, la reaction se produit déja, bien qu' avec lenteur à la temperature de la naphthalene bouillante (280°) et avec une extréme rapidité à 440°."[2]

Now the chlorides of these rare elements enter into reaction

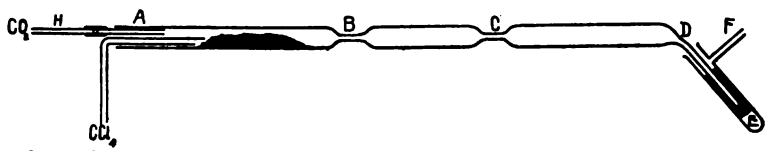
[1] *Compt. Rend.*, 104, 111, *1887*.

[2] *Loc. cit.*

very readily, and may serve as the starting points for numerous syntheses. Demarcay's statements led us to believe that the reaction in question would furnish a rapid method of obtaining these chlorides in quantity with comparative ease. On making use of the method, however, we found that the reaction does not take place in just the way indicated by Demarcay. We will first communicate our results obtained with niobic acid.

We used niobic pentoxide obtained from recrystallized potassium oxyfluosalt resulting from treatments of samarskite. The salt was decomposed in the usual way by sulphuric acid, boiled with water, and the residue ignited at strong red heat to expel the last traces of sulphuric acid.

The oxide was placed in one end of a piece of hard glass tubing, constricted in several places (Fig. 1), and the tube was heated in the vicinity of the oxide in a combustion furnace to



300°–400°. When the vapor of carbon tetrachloride was passed over the heated oxide, a reaction occurred immediately, and a yellowish white sublimate condensed in the cooler parts of the tube. If the oxide employed was quite pure, almost the totality of it could be converted into the volatile product. By careful application of heat it was possible to drive the sublimed substance into the further portions of the tube; it was then seen that the sublimate could be separated into two main portions, a more volatile one of a yellow color, and a less volatile one of a nearly white color. The properties of the yellow product were those of the pentachloride of niobium, while the properties of the whitish portion agreed with those of the oxychloride of niobium. By far the larger portion of the product of the reaction consisted of the oxychloride. The action of carbon tetrachloride on niobic acid seems to yield principally the oxychloride of niobium as the solid product; of the gaseous products formed, phosgene seemed to predominate.

It was thought that possibly the presence of even a slight

amount of air might exercise an oxidizing influence upon the pentachloride at the moment of its formation, converting it into the oxychloride. We accordingly carried out the same experiment in an atmosphere of carbon dioxide, but could not see that the proportion of the pentachloride was at all increased.

Again it was considered that the relative amount of the pentachloride might be made greater by allowing the reaction to take place in an atmosphere of chlorine, but even under such conditions the principal product was found to be the oxychloride.

We conceive then that the main reaction of carbon tetrachloride and niobic pentoxide may be represented by the equation

$$3CCl_4 + Nb_2O_5 = 2NbO.Cl_3 + 3COCl_2,$$

which illustrates again the tendency that niobium has to enter into combination as *niobyl*.

We have prepared a considerable quantity of niobyl chloride according to the above reaction, and, after numerous experiments, have adopted the following method of conducting the operation:

A tube of the shape indicated in the figure is prepared and filled with niobic pentoxide between *A* and *B*. As the chlorine compounds of niobium are quite voluminous, care has to be taken not to employ too much of the oxide; we found that for a tube of about two cm. bore and having a length of about forty cm. between *A* and *B*, ten to fifteen grams could be taken. The tube is placed in a combustion furnace and the portion in the vicinity of the oxide heated to about 400°. A current of dry carbon dioxide is now passed through the tube to dry it thoroughly and expel the air. The constrictions at *B* and *C* are heated nearly to redness to prevent their becoming stopped up, and carbon tetrachloride is gently distilled over upon the niobium compound. It is advisible to discontinue the current of carbonic acid by pinching the delivery tube together at *H*, since often the pressure of the tube becomes sufficient to throw the acid out of the generator. In the early stages of the operation, there occurs a transportation of substance in such a fine state of division that it is carried clear through the tube; in

order to prevent its entering the wash bottle containing sulphuric acid, and connected at *F*, a little glass wool or asbestos fiber is packed around the end of the tube in *E*. When *BC* becomes nearly filled with the products of the reaction, it is heated to a temperature just sufficient to volatilize the pentachloride, which may then be driven over into *CD*, leaving almost pure oxychloride in *BC*. When the reaction is at an end, no more carbon tetrachloride is passed into the tube, but the current of carbon dioxide is again sent through it in order to aid in the separation of the pentachloride from the oxychloride of niobium. Any carbon tetrachloride that may have condensed in *CD* is driven over into *E*, and *BC* and *CD* are so heated that the pentachloride passes through the constriction *C* and condenses just in front of *D*. While it is possible to drive almost all of the pentachloride out of *BC* and thus to obtain almost pure oxychloride, there is always a not inconsiderable portion of the latter compound that finds its way into *CD*.

In several experiments we found that a small quantity of an orange-colored sublimate collected at the further end of *CD*, which circumstance proves that this substance is more volatile than the pentachloride of niobium. H. Rose[1] also observed the formation of such a colored product when he was engaged in the investigation of chlorine on an intimate mixture of charcoal and tantalic acid. He found that if the acid employed contained "nur die geringste Spur von Wolframsäure, so zeigt sich bei der Darstellung des Chlorids eine sehr kleine Menge von einem rothem Chloride, das etwas flüchtiger als das Tantalchlorid ist." The compound is probably the oxytetrachloride of tungsten, its formation being due to a slight contamination of our niobic acid with a tungsten compound.

When we passed the vapor of tetrachloride over tantalic acid, no reaction took place at a lower temperature than 400°, when a small amount of volatile substance was formed, which soon ceased, however. Even on heating to a temperature high enough to cause the Bohemian glass tube to soften, we did not obtain any more of the sublimable product. The tantalic oxid turned yellow and assumed a pasty condition. It is probable that the

[1] *Ann. chem. phys.*, *Pogg.*, 99, 75, *1856*.

sublimed substance consisted of the chlorine compounds of niobium, since it is quite possible that our tantalic oxid was not entirely free from an admixture of niobic oxid. This behavior suggests a method of purification of tantalic acid containing a little niobic acid; we will not lay much stress on this, however, untll we have done more work on the subject.

The readiness with which niobium oxychloride was formed in all our experiments contrasting with the comparatively small quantity of the pentachloride obtained illustrates once again the great inclination niobium has to enter into combination not as an individual element, but in the form of the radical *niobyl*. The action of sulphur and chlorine on NbO, investigated by Delafontaine, the numerous series of oxyfluo-salts prepared by Marignac, and the decomposition of niobyl chloride by magnesium are other facts of the same import. In this respect the analogy of niobium aud vanadium is very striking, but it is almost entirely lacking in niobium and tantalum.

THE CHEMICAL NATURE OF DIASTASE.[1]

SECOND PAPER.

By Thomas B. Osborne and George F. Campbell.

Received May 15, 1896.

In a former paper, by one of us,[2] the results of some attempts to isolate diastase have been detailed. This work has been continued, but as yet no preparations of diastase have been realized more active than those there described. The results given in the former paper, however, have been confirmed, and details of the process for obtaining highly active diastase have been determined more exactly.

Here follows a concise account of this later work so far as it is worth placing on record.

Fifteen kilograms of fine ground malt were treated with thirty liters of five per cent. sodium chloride brine, and after standing some time, with frequent stirring, the extract was pressed out and filtered, yielding sixteen liters of clear filtrate. The meal residue was again treated with fifteen liters of five per cent. brine

1 From the Report of the Connecticut Agricultural Experiment Station for 1895.

2 Eighteenth Annual Report of this Station, pp. 192–207; *J. Am. Chem. Soc.*, 17, 587–603.

and fifteen liters more of clear extract obtained. The united solutions were then saturated with ammonium sulphate and the precipitate filtered out, dissolved in brine and filtered perfectly clear. This liquid was saturated with ammonium sulphate, the precipitate was suspended in two liters of water and dialyzed two days. The ammonium sulphate which adhered to the precipitate, at first prevented solution of the substance, but after two days enough sulphate was removed by dialysis to allow the proteid to dissolve. The solution was filtered clear and dialyzed seven days longer. The globulin thus precipitated was filtered out and the solution, which measured 5800 cc., was dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours. The precipitate, VI,[1] was filtered out and the solution, which then measured 3500 cc., was again dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours yielding precipitate VII. The filtrate from VII measured 2700 cc. and was dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours, giving precipitate VIII, the filtrate from which measured 2000 cc. and was dialyzed into 2500 cc. of alcohol of 0.82 sp. gr. for eighteen hours. This gave precipitate IX, the filtrate from which measuring 1800 cc. was dialyzed into twice its volume of alcohol of 0.81 sp. gr., giving precipitate X. The solution filtered from X was then treated with absolute alcohol until nothing further separated, giving precipitate XI.

These six fractions were all, separately, treated with water; X and XI dissolved completely, the others partially. The aqueous solutions, filtered clear, containing the proteoses and albumin of the six fractions, were then separately dialyzed into water, to remove all freely diffusible substances and, as no globulin was precipitated from any of them, the dialyzers were transferred to alcohol, in order to concentrate their contents, and absolute alcohol was finaly added until the proteids were completely thrown down.

In this way six preparations were obtained, which, when dehydrated with absolute alcohol and dried over sulphuric acid, weighed respectively, 18, 1.37 gram; 19, 1.47 gram; 20, 4.05

[1] The precipitates and preparations described in this paper are numbered consecutively with those specified in the former article on Diastase: This Journal, 17, 587.

grams; 21, 4.82 grams; 22, 2.17 grams; and 23, 0.63 gram.

The disastatic power of these preparations was determined in the manner described in the former paper,[1] and found to be as follows: 18 — 0; 19 = 60; 20 = 300; 21 = 300; 22, trace, and 23 = 0.

It will be noticed that nearly all the enzyme was thrown down in fractions 8 and 9, which gave preparations 20 and 21. These were but half as active as preparation 15, described in the former paper.

In order to purify this diastase, 20 and 21 were united, dissolved in 100 cc. of water, the insoluble matter filtered out and washed with thirty-five cc. of water (these first washings being added to the filtrate), then with more water, and finally with absolute alcohol. Dried over sulphuric acid, this preparation, 24, weighed 0.23 gram. The filtrate and first washings from 24 were treated with 200 cc. of alcohol of 0.885 sp. gr., making a solution containing 36.5 per cent. of alcohol. A small precipitate resulted, 25, which when filtered out and dried over sulphuric acid, weighed 0.25 gram, and had a diastatic value of 15. The filtrate from this precipitate was mixed with 160 cc. of alcohol of 0.84 sp. gr., raising the per cent. of alcohol to 50.7, and the precipitate, 26, thus produced when dried as usual weighed 2.35 gram and had a diastatic value of 86. To the filtrate from 26, 100 cc. of alcohol of 0.84 sp. gr. and 100 cc. of absolute alcohol were added, raising the alcohol-content to 61.6 per cent. The precipitate, 27, which resulted, was filtered out, weighed 2.87 grams and had a diastatic value of 600, just twice that of 20 and 21, from which it had been derived, and just equal to that of the most active preparation, 15, of the former paper. To the filtrate 200 cc. of absolute alcohol were added, giving a precipitate, 28, which weighed 1.00 gram and had a diastatic value of 100.

The filtrate from 28 mixed with 200 cc. more of absolute alcohol, gave a precipitate, 29, which weighed 0.40 gram and showed only a trace of disastatic power. The filtrate from 29, mixed with 400 cc. of absolute alcohol, yielded 0.17 gram of substance, 30, that was totally inactive, and the filtrate from

[1] Report of Conn. Expt. Station for 1894, p. 194; *J. Am. Chem. Soc.*, 17, 587.

this when evaporated to dryness left a residue weighing 0.65 gram.

The results of this experiment showed that little diastase was precipitated by bringing the alcohol-content of the malt extract to fifty per cent. by weight, while nearly all the diastase was thrown down, under the conditions described, when the proportion of alcohol in the malt extract was made sixty per cent.

In order to still further concentrate or purify the diastase contained in precipitate 27, this was treated with 100 cc. of water and, without filtering from the substance which had been coagulated by precipitation and drying, 100 grams of absolute alcohol were added. The precipitate so produced was filtered out and extracted with water. The insoluble matter, after washing and drying, weighed 0.50 gram. The aqueous filtrate, from this insoluble matter, was then completely precipitated with absolute alcohol and 0.45 gram of substance, 31, obtained having a diastatic value of 200. The solution, filtered from the first precipitate, produced by adding an equal weight of alcohol to the solution of 27, as just described, was mixed with enough absolute alcohol to raise this ingredient to fifty per cent., and the substance thereby thrown down, 32, weighed, when dry, one gram, and had a diastatic value of 400. The filtrate from 32 was completely precipitated with absolute alcohol and yielded two-tenths gram of inactive proteid. It is thus seen that the diastase instead of increasing in power under this treatment declined to two-thirds of its original in activity.

Having thus learned more exactly the conditions under which diastase may be so far separated from the other malt proteids, an attempt was made to prepare a large quantity of material with which to carry the purification farther. Through the kindness of Mr. C. Von Eggloffstein, of the Maltine Manufacturing Company, at Yonkers, N. Y., a considerable supply of malt extract, rich in diastase, was placed at our disposal. For this favor and much information respecting malt extracts, we wish to express our especial thanks.

One gallon (3,785 cc.) of this malt extract, which had been concentrated at a low temperature *in vacuo* until it contained about fifty per cent. of solid matter, was dialyzed into water for

forty-eight hours, whereby a large part of the sugar was removed and a thin liquid remained. This was saturated with ammonium sulphate and the precipitated proteids were filtered out, suspended in water and dialyzed for five days. To the liquid contents of the dialyzer, filtered clear from insoluble matters, alcohol was added to make fifty per cent. of the resulting mixture. This threw down a precipitate which was filtered out, dehydrated with absolute alcohol, and dried over sulphuric acid.

This white, easily-powdered precipitate, XII, weighed ninety-five grams. One-half of it was insoluble in water and salt solution. By extraction with water and precipitation with alcohol, added first to fifty per cent. and afterward to sixty per cent., two preparations, 33 and 34, resulted, weighing respectively 4.85 grams and 7.21 grams, that had little diastatic power.

The solution from which the first precipitate, XII, had been separated was treated with enough alcohol to make seventy-five per cent., and the resulting precipitate, XIII, filtered out and found to weigh, when dried over sulphuric acid, seventy grams. This precipitate included the chief part of the diastase of this extract. It dried to a light, dusty powder of pale straw-yellow color, almost entirely soluble in water and had a diastatic value of 200.

XIII was dissolved in water and fractionally precipitated, but, for some unknown reason, the resulting fractions were almost entirely inactive.

In another attempt to make a large quantity of diastase, three gallons (11.4 liters) of the highly concentrated malt extract were mixed with half their weight of water and enough alcohol to make a mixture containing forty-six per cent. of alcohol. A very large precipitate, XIV, resulted, which was filtered out, and as it consisted almost entirely of insoluble matter (probably globulin), it was not further examined.

The filtrate from precipitate XIV was treated with alcohol, raising the strength to sixty per cent; the precipitate so produced was filtered out and, as it contained a large amount of sugar, it was dissolved in about five liters of water, the resulting solution was saturated with ammonium sulphate, the precipitate filtered out, suspended in one liter of water and dialyzed

for five days. The precipitate in the dialyzer was filtered out and the clear solution was treated with alcohol sufficient to make fifty per cent. of the resulting mixture, but as only a little substance separated, the amount of alcohol was increased to sixty per cent. This threw down a considerable precipitate, XV, which, when dehydrated with absolute alcohol and dried over sulphuric acid, weighed fifty-seven grams and had a diastatic value of 300.

Numerous attempts were made to obtain from portions of precipitate XV, by fractional precipitation with alcohol, diastase of greater power than 300, but without success.

Several hundred trials were made with the object to determine precisely the influence of certain conditions, such as the age of the diastase solution, and of certain substances, added in systematically varied quantities, especially sodium chloride, disodium orthophosphate, tripotassium orthophosphate, orthophosphoric acid, acetic acid, and citric acid (using the amount of copper reduction as the measure of effect), but, while the results were decisive in some cases, *e. g.*, citric acid, in the minutest quantities, always depressed or destroyed diastatic action, in the majority of instances, no such uniform results were attainable as would lead to safe conclusions in regard to the circumstances that insure a high degree of diastatic activity.

From our experience in testing these preparations it would seem that the purer the diastase is made, the more sensitive it is to external conditions, and that the method of testing the purity of the ferment by its maltose-producing power thus becomes of uncertain value and perhaps fails to furnish a safe criterion of the purity of the enzyme. That the proteid is not the only factor involved in the amylolytic action of diastase is indicated by the great influence on its activity that often accompanies the addition of various substances to its solution. In view of these facts it is not at all improbable that in thus attempting to purify diastase we remove some substance that favors, or is essential to its action, and that we may have in hand what may be properly termed the enzyme itself, which is feeble in its operation through the absence of deficiency of some accessory substance. Thus the addition of sodium chloride in

many cases increases the diastatic action several fold. That the albumin is an essential factor in diastatic action could not be positively proved, but the results of further experience have tended to strengthen this belief. Of all the preparations that we have made, none from which albumin was absent showed amylolytic power, and those containing the most albumin were the most active. It was always possible to roughly judge of the diastatic power of a preparation, by heating a portion of its solution to 65° C. and observing the amount of coagulum formed.

The fact that active diastase was obtained only from solutions whose alcohol content lies between fifty and sixty per cent., may, we think, be regarded as probable evidence that the enzyme is not something carried down mechanically with the proteid.

THE PROTEIDS OF MALT.[1]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 15, 1896.

AS is well known, water extracts a considerable quantity of proteid matter from ground malt. This we find to consist of at least five distinct bodies, namely, a globulin, an albumin and three proteoses. Whether true peptones are present was not determined, for the malt extracts are so strongly colored that the biuret test entirely fails. Besides the proteids soluble in water another exists that may be taken up by dilute alcohol (of 0.9 sp. gr.). After extracting malt with saline solutions and alcohol, a further quantity of proteid matter remains, the nature of which we have not been able to determine.

Malt-Globulin.—Ten kilograms of air-dried malt, freshly prepared by ourselves in the laboratory, and ground to a fine meal were treated with twenty liters of water and, after standing three hours, were squeezed out in a press and the solution filtered clear. The residual meal was treated with eight liters more of water and the second solution was pressed out and filtered. The united solutions were saturated with ammonium sulphate, the precipitate was suspended in about four liters of water and dialyzed for three days, when it dissolved, with the exception of a

[1] From the Report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

slight residue. In order to reduce its volume and separate impurities, the filtered solution was again saturated with ammonium sulphate, the precipitated substance was suspended in 1500 cubic centimeters of water and dialyzed until the greater part of the ammonium sulphate had been removed, when the solution was filtered clear. The matters now remaining undissolved were treated with ten per cent. salt solution to extract any soluble globulin which might have been deposited during dialysis, and the substance not taken up in salt-solution was filtered out. This last unquestionably consisted almost entirely of insoluble globulin, but as it separated from an unfiltered solution and was small in quantity it was not further examined. The salt-solution was then dialyzed free from chlorides, and the globulin thus precipitated was filtered out, washed with alcohol and dried over sulphuric acid. But 0.5 gram of substance was obtained which, dried at 110°, gave 0.93 per cent. of ash and, reckoned ash-free, 15.70 per cent. of nitrogen. This was marked preparation 1.

The solution of the ammonium sulphate precipitate, containing the bulk of the malt-proteid, from which the insoluble matter yielding preparation 1 had been filtered, was dialyzed, first, into water, until the salts were mostly removed, and then into an equal volume of alcohol of 0.84 sp. gr. for forty-eight hours. The proteid thus precipitated was filtered out and the filtrate was dialyzed into alcohol. After filtering out the second precipitate, the filtrate was dialyzed into stronger alcohol, and this process was repeated, thus depositing the proteids in four fractions, a fifth being obtained by adding absolute alcohol to the remaining solution as long as anything was thrown down. Each of these five fractions was then treated with water to dissolve albumins and proteoses and the resulting solutions were dialyzed in water for several days. The first four fractions were but partly soluble in water, and accordingly, the insoluble parts, after washing with water, were treated with ten per cent. sodium chloride solution, and the portion which in each case remained undissolved was filtered out, washed thoroughly with water and alcohol and dried at 110° for analysis. The four saline extracts were then dialyzed, bnt those from the third and fourth fractions were

found to contain only trifling quantities of proteids. That from the second fraction gave no precipitate of globulin on dialysis, but by adding alcohol to the solution 0.49 gram of preparation 2 was obtained, having 4.33 per cent. of ash and, calculated ash-free, 15.18 per cent. of nitrogen. The sodium chloride extract from the first fraction gave a precipitate on dialysis which, after washing with water and with alcohol, weighed one and two-tenths grams, 3.

The filtrate from 3, by precipitation with alcohol, yielded 4, weighing 1.54 grams.

After extracting the four fractional precipitates with water and with salt solution, the undissolved residue, in each case, was washed thoroughly with salt solution, with water and with alcohol and dried over sulphuric acid, giving, in the order named, preparation 5 weighing eight grams, 6 weighing five grams, 7 weighing 2.87 grams, and 8 weighing nine-tenths gram. These preparations, dried at 110°, had the following composition:

MALT-GLOBULIN, BYNEDESTIN.

	3.	4.		5.	6.	7.	8.
Carbon....	53.11	53.58		53.55	53.51	53.25	53.42
Hydrogen.	6.45	6.70		7.01	6.75	....	7.15
Nitrogen..	15.78	15.86	15.87	15.72	15.87	16.12	16.65
Sulphur Oxygen	24.66	23.86		1.23 22.49	1.12 22.75	1.38	22.78
	100.00	100.00		100.00			100.00
Ash......	0.75	1.43		1.09	0.66	0.55	0.24

Preparations 5 and 6 have the same composition as the globulin 3 and 4 obtained from the sodium chloride extracts of the fractional precipitates, while 8 contains nearly one per cent. more nitrogen, and as will be seen later, has nearly the same composition as malt albumin and is unquestionably for the most part albumin coagulated by the action of the alcohol. 7 appears to be a mixture of coagulated globulin and albumin. In a similar manner three other preparations of the coagulated globulin 9, 10 and 11 were obtained from another lot of malt.

MALT-GLOBULIN, BYNEDESTIN.

	9	10	11
Carbon	52.90	52.99	53.15
Hydrogen	6.74	6.64	6.52
Nitrogen	15.33	15.31	15.81
Sulphur	1.17	25.06	1.47
Oxygen	23.86		23.05
	100.00	100.00	100.00
Ash	0.44	0.32	0.23

Preparations 9 and 10 are lower in carbon and nitrogen than those just described, probably because, having been prepared in a smaller quantity, they carried down a larger proportion of impurities when thrown out of solution by alcohol.

From a malt extract that had been concentrated *in vacuo* at a low temperature, for which we are indebted to Mr. C. von Egloff-stein, alcohol, added to make forty-six per cent. by weight of the mixture, threw down a large quantity of coagulated globulin that was not further examined, the filtrate from which, on increasing the content of alcohol to sixty per cent., gave a second precipitate that was largely soluble in water. It was accordingly mixed with water and with ammonium sulphate in excess, and the substance thus thrown down was suspended in a liter of water and dialyzed for five days. The insoluble residue in the dialyzer, when washed with water and alcohol, gave preparation 12, weighing 26.78 grams. From this same extract by fractional precipitation with alcohol another small preparation of coagulated globulin, 13, was obtained.

SUMMARY OF ANALYSES OF MALT-GLOBULIN, BYNEDESTIN.

	1	2	3	4	5	6
Carbon			53.11	53.58	53.55	53.51
Hydrogen			6.45	6.70	7.01	6.75
Nitrogen	15.70	15.18	15.78	15.86	15.72	15.87
Sulphur					1.23	1.12
Sulphur and Oxygen			24.66	23.86		
Oxygen					22.49	22.75
			100.00	100.00	100.00	100.00

	9	10	11	12	13
Carbon	52.90	52.99	53.15	53.04	52.96
Hydrogen	6.74	6.64	6.52	6.57	6.83
Nitrogen	15.33	15.31	15.81	15.94	15.96
Sulphur	1.17		1.47		
		25.06			
Oxygen	23.86		23.05	23.61	24.25
	100.00	100.00	100.00	100.00	100.00

Although considerable differences exist among these analyses, they agree with each other as well perhaps as could be expected considering the difficulty of preparing the substance in a state of purity.

Whether other globulins occurred in the malt could not be determined by fractional precipitation owing to the small total quantity of globulin present.

The malt residue remaining after extracting with water, in the case first described, was treated with ten per cent. salt solution and the clear filtered liquid was dialyzed until free from chlorides. The precipitated globulin was filtered out, washed with water and alcohol and dried over sulphuric acid. This preparation, 14, weighed 4.12 grams and had the following composition :

MALT-GLOBULIN, BYNEDESTIN.

	14		
	I.	II.	Average.
Carbon	52.94	52.78	52.86
Hydrogen	6.87	6.79	6.83
Nitrogen	16.16	16.18	16.17
Sulphur	1.14		1.14
Oxygen			23.00
			100.00
Ash	0.96		

It is to be noted that the carbon is a little lower and the nitrogen higher than the average of the figures previously obtained. This is perhaps due to presence of a little edestin,[1] the globulin of ungerminated barley. Edestin is not readily soluble in dilute saline solutions, such as are formed on treating seeds with water, and, if occurring in the malt, ought to be present in the salt extract of the meal after it has been exhausted with water.

[1] Annual Report of Conn. Agr. Expt. Station for 1894, p. 172, and Journal of American Chemical Society, 17, 545.

Owing to the incomplete extraction with water, the preparation obtained in this case should be a mixture of the two globulins, if both are present. Edestin can only occur in extremely small quantity in malt, since but 4.12 grams of globulin were obtained by extracting ten kilograms of malt with salt solution after treatment with water, and most of this consisted of the more soluble globulin first described. It is interesting to note the practically complete disappearance of edestin during germination and the formation of the more soluble globulin with three per cent. less nitrogen and two per cent. more carbon. It is, of course, not demonstrated that the malt globulin is derived from edestin, but that the proteids undergo extensive changes before conversion into proteoses and peptones is very evident.

When dissolved in considerable quantity in salt solution, bynedestin is precipitated by water, is not precipitated by saturation with sodium chloride, and but partly by saturation with magnesium sulphate. With the biuret test it gives a violet color. Dissolved in ten per cent. sodium chloride solution and heated to 65°, a turbidity is produced which increases to flocks at 84°. The coagulum gradually augments as the temperature rises but, after heating to 100°, the filtrate from the coagulum yields an abundant precipitate on adding dilute hydrochloric acid. The solution in ten per cent. sodium chloride brine gives a precipitate with acetic acid which is soluble in an excess of the acid. These reactions show that this body is in no sense a proteose, but has characters common to plant globulins. Bynedestin formed about sixty per cent. of the total water-soluble proteid matter in the malt extract first described in this paper. Out of a total of 33.27 gram of proteid recovered in the different preparations from 10,000 grams of malt, 19.88 grams consisted of bynedestin.

Malt Albumin, Leucosin.—Under the name leucosin, one of us has described an albumin occurring in small quantity in the seeds of wheat, rye and barley. In the aqueous malt-extracts an albumin is found identical wlth leucosin in properties and composition. As stated in previous papers, this albumin is so intimately associated with diastatic action as to make probable that it is either diastase itself or an essential factor in diastatic

amylolysis. In attempts to fractionally separate malt-leucosin from the associated proteids, many preparations have been made which are mixtures of leucosin with proteose. In several cases these mixtures have been analyzed and have so nearly the composition of leucosin as to make certain that one of the proteoses of malt has very nearly the same ultimate composition as the albumin. Analyses of these mixtures may therefore be taken to represent the composition of either of these proteids.

In the extraction first described in this paper, two preparations, 15 and 16, of albumin coagulated by alcohol, were obtained from solutions out of which the globulin had been precipitated by alcohol. If, as is invariably assumed, proteose cannot be rendered insoluble by contact with alcohol, these preparations may be taken to represent the composition of malt albumin. Their composition is here compared with that of leucosin coagulated by heat.

LEUCOSIN.

	Malt. 15	Malt. 16	Wheat, rye and barley. Average.
Carbon	53.23	52.90	52.93
Hydrogen	6.64	6.79	6.80
Nitrogen	17.00	16.41	16.70
Sulphur }	23.13	23.90	1.37
Oxygen }			22.20
	100.00	100.00	100.00
Ash	0.84	0.55	

The following figures give the composition of preparations derived from three different samples of malt. These were all obtained by precipitating the proteids with ammonium sulphate, dissolving the precipitates in water, dialyzing away the greater part of the salt and fractionally precipitating the solutions with alcohol. The fractions were dissolved in water as far as possible, filtered from the undissolved globulin and the aqueous solutions dialyzed for several days in water and then in alcohol. The proteids thus precipitated were mixtures of proteose and albumin. It will be noted that they all agree fairly well with one another and with leucosin in composition. Since these mixtures contained

from six and a half to fifty per cent. of albumin, it is evident that the two proteids have a very similar composition.

MALT LEUCOSIN AND PROTEOSE.

	17	18	19	20	21	22	23	24
Carbon	53.16	53.19	52.80	52.50	52.38	52.85	52.61	52.55
Hydrogen	7.03	6.71	6.96	6.72	6.63	6.67		
Nitrogen	16.50	16.60	16.09	16.10	16.51	16.25	16.35	16.41
Sulphur	23.31	1.38	1.45	24.68	24.48	24.23		
Oxygen		22.12	22.70					
	100.00	100.00	100.00	100.00	100.00	100.00		
Ash	0.84	0.78	0.59	0.66	1.55	0.22	0.51	

The preparations containing the most albumin, when dissolved in water, became turbid on heating to 50° and formed flocculent coagula at 58°. By saturating their solutions with magnesium sulphate the albumin was completely thrown out, and together with it much of the proteose. Saturating solutions of these preparations with sodium chloride, gave no precipitate when they contained but little albumin, but a heavy precipitate appeared on adding acetic acid to the salt-saturated solution. Solutions of the preparations containing much albumin gave precipitates on saturating with sodium chloride.

PROTEOSES OF MALT.

The proteose associated with albumin has the properties of a *protoproteose*, since it is readily and abundantly precipitated from its salt-saturated solution on adding acetic acid.

When malt extract is fractionally precipitated with alcohol a considerable quantity of proteose is thrown down before the albumin, so that the water-soluble part of the first fraction is chiefly proteose. The proportion of albumin in the precipitates increases as the alcohol is made stronger up to the point where it is all precipitated. At this stage much proteose remains dissolved which behaves differently from that first thrown down. A large quantity of concentrated malt extract was precipitated by alcohol added to 60 per cent., and after filtering, the proportion of alcohol was raised to seventy-two per cent. The substance thereby precipitated, when dried over sulphuric acid, weighed thirty-eight grams. This was dissolved in water, the solution was heated to boiling,

the coagulated albumin was filtered out and twenty per cent. of sodium chloride added to the solution. This caused a slight precipitate which was evidently the alcohol-soluble proteid, to be described later. The filtrate from this substance was then treated with a little acetic acid, which produced a copious precipitate that was filtered out and dissolved in water. This solution, exactly neutralized with sodium carbonate and fully saturated with salt, yielded a considerable precipitate, which was filtered out, dissolved in water and dialyzed free from chlorides.

A very small deposit, consisting of minute spheroids, was found in the dialyzer. This dissolved readily in exceedingly dilute salt solution, from which it was thrown down by much water. On adding nitric acid to the solution of this substance a precipiate was produced that dissolved on warming and reappeared on cooling, gave a clear pink biuret reaction and was precipitated by copper sulphate. On boiling its solution not even a turbidity was produced. Except for its behavior on heating, this substance has all the reactions of a *heteroproteose*. The amount obtained was exceedingly small, only enough for the above reactions. The solution filtered from this heteroproteose was concentrated by gently boiling over a low flame.

During concentration of the solution filtered from the heteroproteose a coagulum developed as a film on the surface of the liquid and sides of the dish. We have frequently noticed that plant proteoses from various seeds coagulate in this manner although behaving in most other respects like typical proteose. This coagulum, 25, filtered out washed with water and alcohol and dried over sulphuric acid, weighed 0.29 gram and contained 16.84 per cent. of nitrogen.

The filtrate from 25 was precipitated by alcohol and gave 1.45 gram of 26, having the following composition, when dried at 110°:

MALT PROTEOSE, 26.

	I.	II.	Average.
Carbon	50.61	50.64	50.63
Hydrogen	6.72	6.61	6.67
Nitrogen	16.69	....	16.69
Sulphur } Oxygen }	....	....	26.01
			100.00
Ash	....	....	1.29

As will be remembered, in making these preparations, 25 and 26, the proteose was precipitated, first, by adding acetic acid to the solution containing twenty per cent. of salt and, second, by dissolving the precipitate thus produced in water and saturating the neutralized solution with salt. The filtrate, A, from the first, as well as the filtrate, B, from the second precipitation, still contained proteose.

A was therefore neutralized with sodium carbonate and saturated with salt, but, as no precipitate resulted, acetic acid was added as long as any proteid was thrown down.

B was treated similarly with acetic acid and the two precipitates thus obtained from the salt-saturated solutions were collected on the same paper and the filtrates were united and marked C. The precipitates were dissolved in water, the solution carefully neutralized, dialyzed free from chlorides and then concentrated by slow boiling. During concentration a small coagulum separated which was filtered out, washed with water and alcohol and dried over sulphuric acid. This preparation, 27, weighed 0.22 gram and contained, without correcting for ash, 16.40 per cent. of nitrogen.

An excess of alcohol was added to the filtrate from 27, and the precipitate produced, after treating in the usual manner, gave 1.49 gram of preparation 28, which, dried at 110°, had the following composition:

MALT PROTEOSE, 28.

	I.	II.	Average.
Carbon	49.82	49.87	49.85
Hydrogen	6.69	6.64	6.67
Nitrogen	16.00	....	16.00
Sulphur, Oxygen	....	....	27.48
			100.00
Ash	....	....	1.54

The salt-saturated filtrate, C from which 27 and 28 had been precipitated, was neutralized and dialyzed until much of the salt had been removed, then concentrated and dialyzed until free from chloride. The solution was finally concentrated to small volume and precipitated with alcohol. The substance so

obtained, after treating as usual, weighed 6.25 grams but was found to contain 4.70 per cent. of ash and only 8,91 per cent. of nitrogen, reckoned ash-free. This precipitate, which was expected to contain *deuteroproteose*, evidently included much non-proteid matter.

It will be noticed that of the thirty-eight grams of substance taken, only a very small part was recovered. It is probable that a large share of the substance (p. 550) was non-proteid, and also that during the dialysis much proteose was lost by diffusion.

Preparation 26 has the properties of a protoproteose and may be regarded as such. Preparation 28 is a mixture of proto- and deuteroproteose. Pure deuteroproteose was not obtained, it having been impossible to separate the non-proteid substances associated with it.

It thus appears that at least two protoproteoses exist in malt, for 26 has much less carbon than the mixtures of proteose and albumin, 17 to 24. Preparation 17 contains about ninety-five per cent. of proteose and has 53.16 per cent. of carbon, whereas 26 has only 50.63 per cent. of carbon. This difference can scarcely be due to non-proteid impurities, for 26 contains even more nitrogen than 17. According to the definitions now accepted, a protoproteose is any form of proteid which is soluble in pure water, uncoagulable by heat, precipitable by saturation with sodium chloride, and gives a pink biuret reaction and a precipitate with nitric acid that dissolves on warming and reappears on cooling. The protoproteoses obtained by artificial digestion, usually have a composition varying with that of the proteids from which they are derived, and the proteoses of malt may also be expected to differ according as they originate from one or another of the several proteids of barley. While the plant proteoses resemble the digestive proteoses in the reactions just specified, some of their physical properties are so different that it is not improbable that they are quite distinct substances.

MALT PROTEID SOLUBLE IN DILUTE ALCOHOL. BYNIN.

Three kilograms of ground malt were extracted with alcohol of 0.90 sp. gr. The extract was filtered clear, and concentrated to about one-third its original volume, on a water bath.

When cool the solution was poured off from the separated proteid and the latter was washed with dilute salt solution, with water, with ether to remove adhering water, and finally with absolute alcohol. Dried over sulphuric acid, this preparation, 29, weighed 33.1 grams, being 1.11 per cent. of the malt.

Dried at 110° it had the following composition:

BYNIN, 29.

	I.	II.	Average.
Carbon	55.01	54.93	54.97
Hydrogen	6.77	6.49	6.63
Nitrogen	15.98	16.13	16.06
Sulphur	0.94	....	0.94
Oxygen	....	....	21.40
			100.00
Ash	....	....	0.67

In order to fraction this substance, twenty-seven grams were dissolved in alcohol of 0.70 sp. gr., the solution filtered perfectly clear, concentrated to small volume and poured into absolute alcohol, a few drops of ten per cent. salt solution being added to cause the proteid to separate. The precipitate so produced was filtered out, treated with absolute alcohol and dried over sulphuric acid. This preparation, 30, weighed twenty grams, and when dried at 110° had the following composition:

BYNIN, 30.

	I.	II.	Average.
Carbon	54.74	55.08	54.91
Hydrogen	6.61	6.62	6.62
Nitrogen	16.21	16.06	16.14
Sulphur	0.83	....	0.83
Oxygen	....	....	55.07
			100.00
Ash	....	....	0.40

Of preparation 30, sixteen grams were dissolved in 180 cc. of warm alcohol of fifty per cent. by volume, and a part of the proteid precipitated by cooling to 0° C. The solution was decanted and the precipitate, 30*a*, was treated as just described for 30. The substance now separated, 30*b*, was treated in the same manner. 30*c*, thus obtained, was dissolved in a little strong

alcohol and the perfectly clear solution poured into absolute alcohol, adding also a few drops of ten per cent. salt solution. The precipitate was then dehydrated with absolute alcohol and dried over sulphuric acid. This preparation, 31, weighed eight and three-tenths grams and gave the following results on analysis:

BYNIN, 31.

	I.	II.	Average.
Carbon	55.07	....	55.07
Hydrogen	6.75	....	6.75
Nitrogen	16.18	16.42	16.30
Sulphur	0.84	....	0.84
Oxygen	....	....	21.04
			100.00
Ash	....	....	0.10

The solutions containing fifty per cent. of alcohol, which had been decanted from 30*a*, 30*b* and 30*c* were united, concentrated to small volume, cooled, and the liquid poured off from deposited substance. The latter, dehydrated with absolute alcohol and dried over sulphuric acid—preparation 32—weighed five grams.

As seen from the following table, these analyses show that the proteid has not been separated into fractions of differing composition.

SUMMARY OF ANALYSIS OF BYNIN.

	29.	30.	31.	32.	Average.
Carbon	54.67	54.91	55.07	55.16	55.03
Hydrogen	6.63	6.62	6.75	6.67	6.67
Nitrogen	16.06	16.14	16.30	16.53	16.26
Sulphur	0.94	0.83	0.84	0.76	0.84
Oxygen	21.40	21.50	21.04	20.88	21.20
	100.00	100.00	100.00	100.00	100.00
Ash	0.67	0.40	0.10	0.16	

These figures are, except for hydrogen, in remarkably close agreement with those given by Chittenden and Osborne for the composition of zein, the alcohol soluble proteid of maize; but in properties the two bodies are very distinctly different. Compared with hordein, the alcohol soluble porteid of barley, this malt proteid contains about one per cent. more carbon and one per cent. less nitrogen.

ALCOHOL SOLUBLE PROTEIDS.

	Hordein of barley.	Bynin of barley malt.	Zein of maize.
Carbon	54.29	55.00	55.23
Hydrogen	6.80	6.67	7.26
Nitrogen	17.21	16.26	16.13
Sulphur	0.83	0.84	0.60
Oxygen	20.87	21.20	20.78
	100.00	100.00	100.00

MALT PROTEID INSOLUBLE IN WATER SOLUTION AND DILUTE ALCOHOL.

The proteid remaining undissolved, after extracting malt with water, salt solution and alcohol, was not separated or identified, but its presence in considerable quantity was shown, as follows:

After extracting 100 grams of malt first, with ten per cent. sodium chloride solution, and then with alcohol of 0.90 sp. gr., dehydrating with absolute alcohol and drying in the air, a residue was obtained which weighed seventy-five grams and contained 0.82 per cent of nitrogen, equivalent to 0.62 per cent. reckoned on the original malt. Assuming, as is probably true, that this nitrogen belongs to proteid matter, we have in the residue three and eight-tenths per cent. of proteid, insoluble in the reagents named.

SUMMARY.

In the malt used in this investigation we have found :

1. *Bynedestin*, readily soluble in very dilute salt solution, therefore largely passing into the aqueous extracts because of the soluble salts of the seed. This globulin contains two per cent. more carbon and three per cent. less nitrogen than edestin, the globulin of barley, and is much more soluble in very dilute salt solutions than edestin.

The composition of this globulin, as shown by the average of eleven analyses, is:

BYNEDESTIN.

Carbon	53.19
Hydrogen	6.69
Nitrogen	15.68
Sulphur	1.25
Oxygen	23.19
	100.00

Bynedestin, dissolved in ten per cent. sodium chloride solution, gives a turbidity at 65° and a flocculent coagulum at 84°, but, even after heating for some time at 100°, the coagulation is far from complete.

This proteid is not precipitated by saturating its solutions with sodium chloride, and but partly precipitated by saturating with magnesium sulphate.

2. *Leucosin*, an albumin, identical in composition and properties with the leucosin found in wheat, rye and barley. The composition of this proteid was found to be:

MALT ALBUMIN, LEUCOSIN.

Carbon	53.07
Hydrogen	6.72
Nitrogen	16.71
Sulphur } Oxygen }	23.50
	100.00

Leucosin is intimately associated with diastase.[1] Heated to 59°, solutions of this proteid become turbid, and at 58° a flocculent coagulum occurs. Coagulation, however, is incomplete unless the solution is heated for some time and the temperature raised to about 70°. Saturation with sodium chloride or with magnesium sulphate partly precipitates leucosin.

3. A *Protoproteose* readily precipitated from aqueous solution by adding an equal weight of alcohol. No preparations of this body were obtained free from albumin. Its composition is nearly the same as that of leucosin, since preparations containing from ninety to fifty per cent. of it, together with from ten to fifty per cent. of leucosin, are not distinguishable by analysis.

4. A *Protoproteose* less readily precipitated by alcohol than the preceding, and of a different composition, as shown by the following figures:

MALT PROTOPROTEOSE.

Carbon	50.63
Hydrogen	6.67
Nitrogen	16.69
Sulphur } Oxygen }	26.01
	100.00

[1] See papers on Diastase, Annual Reports of Conn. Agr. Expt. Station, 1894. pp. 202, 204, and 1895, p. 238; also this JOURNAL, 17, 587; 18, 536.

That this is not an impure preparation of the preceding, is indicated by the fact that the amount of nitrogen is alike in both, while the carbon differs by two per cent. This difference would probably not be caused by non-proteid impurities. It is possible that the deuteroproteose next to be described, may not have been completely separated by the process employed.

5. A *Deuteroproteose* which could not be separated from non-proteid impurities.

6. A *Heteroproteose* in extremely small amount.

7. *Bynin* a proteid insoluble in water and saline solutions, but readily soluble in dilute alcohol. About 1.25 per cent. of this proteid was obtained from the malt, having the following composition:

BYNIN.

Carbon	55.03
Hydrogen	6.67
Nitrogen	16.26
Sulphur	0.84
Oxygen	21.20
	100.00

8. A proteid insoluble in water, in salt solution and in alcohol, amounting to 3.80 per cent. The composition and properties of this proteid we have been unable to determine.

PROPORTIONS OF THE VARIOUS PROTEIDS IN MALT.

Assuming twenty-one per cent. of the total nitrogen of the malt to exist in non-proteid bodies, and admitting the malt proteids to contain on the average 16.3 per cent. of nitrogen, we have, in the malt investigated, a total of 7.84 per cent of proteids.

As already indicated, p. 555, proteid equal to three and eight-tenth per cent. of the malt was insoluble in alcohol and in salt solution.

It was shown on page 553 that 1.11 per cent. of proteid was recovered from alcohol solution, and making allowance for loss, we may place the amount of alcohol-soluble proteid at 1.25 per cent.

Subtracting the sum of the insoluble proteid and the alcohol soluble proteid from the total malt proteids, we have 2.79 per

cent. for proteids soluble in salt solution, *viz.*, globulin, albumin, and proteoses.

The amount of coagulable proteids was found to be 1.50 per cent., consisting of albumin and a part of the globulin. There remains then 1.29 per cent. for the uncoagulated globulin and the various proteoses. We have accordingly, in the malt used for these determinations, approximately:

		Per cent.
Proteid, insoluble in salt solution and in alcohol		3.80
Bynin, soluble in dilute alcohol		1.25
Bynedestin, leucosin and proteoses soluble in water and salt solution	Coagulable	1.50
	Uncoagulable	1.29
Total proteids		7.84

The results of this study show: that, in germination, the proteids of barley undergo extensive changes without acquiring, or before acquiring the properties of proteoses; that hordein disappears and an alcohol soluble proteid of entirely different composition takes its place; that edestin also disappears and a new globulin is formed, very different both in composition and properties. The albumin, on the other hand, appears to be unchanged in its characters, but its quantity is increased. It is to be noted also that hordein and edestin are both replaced by proteids much richer in carbon and poorer in nitrogen.

NOTE.

A Cheap Adjustable Electrolytic Stand.—Stands for electrolytic work, especially for efficient assaying of copper, should fulfill certain conditions.

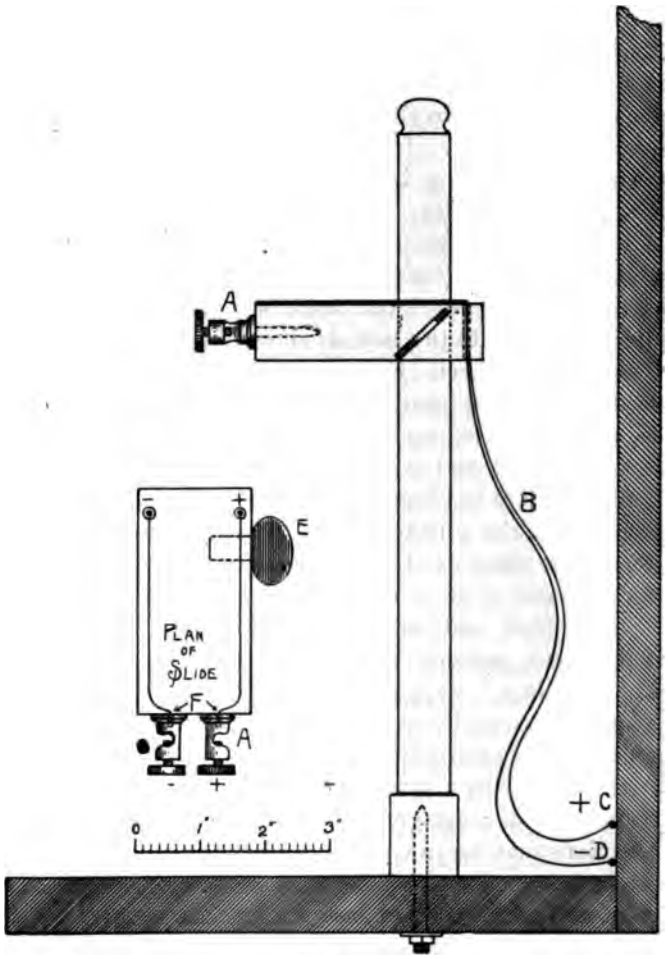
All joints and connections, as far as possible, should be permanently soldered and very few switches used.

If many assays of the same kind are to be simultaneously conducted, each assay should be independent of its neighbor.

The stands or terminals, for holding the platinum cases or cylinders and spirals (which are the forms of electrodes generally used in large laboratories), should be capable of instant adjustment to suit a beaker of any height and size, or permit a block of wood to be placed under the beaker, since some chemists

prefer when an electrolysis is finished, to wash the electrodes by quickly slipping out a block, dropping the beaker, and replacing it with another of distilled water.

The author has designed and used for several years, electro-



lytic stands which are simple in construction and comparatively inexpensive, and a number of them may be quickly turned

out together in any works possessing a carpenter or machine shop.

The drawing shows that the stands each consist of small, turned sticks of oak wood, one foot high, and fastened by a short lag screw, bolt, or common screw and washer, to a wooden shelf one inch thick, under which are placed the gravity or storage batteries.

A block of wood, of the shape and construction given in the sketch, is arranged to slide on the wooden post, and fastened by the large screw (*E*). Into the front end of the sliding block are screwed two brass holders for the "cylinders," or "cone and spiral" electrodes.

All dimensions may be taken from the scale accompanying the sketch. The "single binding posts" given in chemical catalogues, make very good holders if one side of the brass post is filed out opposite the hole as shown in cut (at *A*.)

The cotton-covered (No. 19) connecting wires (*B*) are connected by soldered joints with two parallel main wires (No. 16) at *C*, *D*, and are led up through two small holes at the back of the sliding block and over the top to the brass plugs in front.

These holders or plugs may be screwed in part way, and the bared ends of the wire twisted once around the screw.

The brass plugs are then screwed up tightly in position, the short, free end of the wire bent down over the top in a little slot previously filed, and fastened with a drop of solder (as at *F*.)

These neat, wooden stands may be set in a single or in a double row in a "staggering" position.

The stands may be arranged in little sets of twos or fours, independent of each other, by breaking one of the parallel main wires at *C* or *D* by a switch or removable plug of low resistance.

From each of these groups or sets lead wires with soldered connections may be run to batteries below, and to arrangements of incandescent lamps on the wall above and behind the row of stands, and each group of assays may thus be given a different strength of current, one sixteen candle power lamp being generally sufficient for four copper assays.

The advantage of connecting assays of the same kind in parallel, as indicated in the sketch, consists mainly in the fact

that the current is divided up between the assays, lessening the total resistance, and that any electrode may be quickly removed after loosening the screw at *A* without disturbing the other analyses.

If the laboratory is wired for incandescent (seventy-five volt) lamps, the current obtained from a circuit containing arrangements of sixteen or thirty-two candle power lamps is more steady than that from small batteries.

If the dynamo only runs at night, a bank of lamps in parallel arc may be arranged as a resistance and the current passing through these, caused to charge two or more storage batteries in series at night. In the morning the direct current, through resistance of lamps, which had been applied to analyses during the night, may then be switched off and the dynamo current also switched off from storage cells, which are then connected up, through suitable resistance coils, in an opposite direction with the copper analyses yet unfinished.

As noted, adjustable resistance coils should be included in the circuit of analyses, through which the storage cells discharge. For a description of such apparatus, I refer to the works of well known authorities,[1] [2] and for different arrangements of incandescent lamps to articles in this Journal of 1894 and 1895.

The "chloride accumulator" is thought to be the most efficient storage cell for laboratory work. Three cells in series of the type (5 E, Electric S. Bat. Co., Phila.), require the current of ten sixteen-candle-power lamps in parallel arc to secure a full charge in one night of twelve to fourteen hours, and will, when connected with analyses, give out again for a period of fourteen to fifteen hours about eighty per cent. at two volts potential.

The foregoing descriptions will, it is hoped, be of service to those who have considerable electrolytic work with copper, or other metals, and the stand described is recommended as one that is permanent, easily adjustable and comparatively inexpensive, if set up by the chemist himself.

G. L. HEATH.

[1] Clasen s Quant. Anal. by Elect,, Am. Ed., pp. 23-28.
[2] E. F. Smith's Electrolysis, pp. 27-28.

NEW BOOKS.

WATER SUPPLY (CONSIDERED PRINCIPALLY FROM A SANITARY STANDPOINT). BY WILLIAM P. MASON. 8vo. viii, 504 pp. New York: John Wiley & Sons. Price, $5.00.

There is scarcely a subject about which chemists are called upon to give an opinion, which requires broader knowledge, more care in analytical work and, above all, more exercise of good common sense, than the determination of the sanitary character of a water supply.

The present work will be found of service not only to chemists, but also to physicians, engineers, and many others who are called upon to consider problems of this kind.

The author has had a wide practical experience in the study of water supplies and shows excellent judgment selecting that which is most valuable, both from his own experience and from the almost boundless literature of the subject.

In a long chapter on Drinking Water and Disease, a good selection is given from the many cases on record where epidemics, especially of typhoid fever and of cholera, have been proved to have been connected with the use of a contaminated water.

The chapter on the artificial purification of water gives a detailed account of the best systems in use in America and in Europe for the filtration of water on a large scale. A large number of plants of this character have been personally examined by the author.

In discussing the natural purification of water it is interesting to notice that the author agrees with those who believe that the self-purification of a river water which has once been seriously contaminated with sewage is a very slow process, and that such waters should not be recommended for potable use even after many miles of flow. The evidence given on this point seems to be almost incontrovertible.

About one-third of the book is given to the discussion of the various forms of natural waters: rain, ice, snow, river water, stored water, ground water and deep-seated water.

Concise and satisfactory directions are given for the chemical

and bacteriological examination of waters, the latter being confined to methods of preparing culture liquids and counting colonies. In the opinion of the writer the retort which is recommended for the "albuminoid" ammonia process would be better replaced by a flask, or a distilling bulb with a ground glass stopper. The retort seems to have little place left in the modern laboratory.

The opinion is expressed that, while the bacteriological examination is important, its value has been greatly overrated, and the chemical examination will, in most cases, give more reliable information as to the character of a water.

The typography and general arrangement of the book are excellent, and the writer is not acquainted with any other work which contains so much that is of value on the subject.

W. A. NOYES.

HINTS ON THE TEACHING OF ELEMENTARY CHEMISTRY IN SCHOOLS AND SCIENCE CLASSES. By William A. Tilden, D.Sc., F.R S. London: Longmans, Green & Co. 1895. 12mo. 84 pp. Ill. Price, 75 cents.

Dr. Tilden is one of the English chemists who examines many papers written by candidates in chemistry. He is well qualified, therefore, to speak to teachers of the subject, and his book is practically a series of short talks to teachers. The following extract gives a good idea of his point of view:

"In order to cultivate the powers of observation, various branches of natural science have been brought into use in schools, but none seem to present so many advantages as are offered by chemistry when rightly taught. As a science based entirely upon the results of observation and experiment, it is only by making experiment a principal feature of the system of instruction that these advantages can be secured. The observations and experiments must also, as far as possible, be the work of the pupil and not of the teacher, and therefore exercises undertaken should be in the first instance of the simplest possible character, and graduated so as to lead on to more difficult operations, which should only be undertaken after some time and after demonstration by the teacher. It is a mistake to suppose that the great theories of chemistry can be established by experiments conducted wholly by beginners, but with due preliminary

instruction the more advanced student may get a long way in this direction."

Prof. Tilden seems to fully comprehend the necessity for simplicity in the apparatus to be used by beginners and a number of hints are given in this line worth consideration.

EDWARD HART.

BOOKS RECEIVED.

Bulletin No. 41. Experiments with Wheat and Oats. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 16 pp.

Bulletin No. 42. Corn Experiments. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 18 pp.

Chemistry at a Glance. A Study in Molecular Architecture. By Herbert B. Tuttle. No. 1. Oxides. 1896. 59 pp. Price, 60 cents.

A Dictionary of Chemical Solubilities. (Inorganic.) By Arthur Messinger Comey, Ph.D. London: Macmillan & Co., and New York. 1896. xx, 515 pp. Price $5.00.

Experimental-Untersuchungen über Zersetzung und Verbrennung von Kohlenwasserstoffen. By Fritz Haber. München: R. Oldenbourg. 1896. 116 pp. Price M 1.50.

Elementary Chemistry. By Paul C. Freer. Boston: Allyn & Bacon. 1895. x, 284 pp. Introductory price, $1.00.

Bulletin No. 41. Tobacco. Yellow Leaf and Cigar Varieties. Agricultural Experiment Station, Baton Rouge, La. 32 pp.

Nineteenth Annual Report of the Connecticut Agricultural Experiment Station for 1895. Part II. Fertilizer Experiments. New Haven: Connecticut Experiment Station. 157 pp.

The Liquefaction of Gases. Papers by Michael Faraday, F.R.S., with an appendix. Alembic Club Reprints, No. 12. Edinburgh: Wm. F. Clay. 79 pp. Price, two shillings.

Nineteenth Annual Report of the Connecticut Agricultural Experiment Station for 1895. Part III. Proteids of Potato; of Pea and Vetch; Conglutin and Vitellin. Recent Laws affecting the Station: Index. New Haven, Conn.: Connecticut Agricultural Experiment Station. 88 pp.

VOL. XVIII. [JULY, 1896.] No. 7.

THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

THE VALUE OF LEATHER REFUSE.

BY J. B. LINDSEY.

Received May 14, 1896.

I. RAW, ROASTED OR STEAMED LEATHER.

IN another publication[1] the writer reviewed the experiments made by various investigators concerning the agricultural value of different forms of leather refuse, and drew the following conclusions: "The results of both field and pot experiments, as well as artificial digestion experiments, indicate that leather, either raw, roasted or steamed, is a very inferior source of plant food. Carefully conducted experiments by Wagner give the nitrogen it contains a relative value of 20, the nitrogen in sodium nitrate being valued at 100. When nitrogen in organic matter is valued at from sixteen to eighteen cents per pound, nitrogen in raw, roasted or steamed leather should be worth but from three to six cents per pound.

II. DISSOLVED LEATHER.

Deherain and others have suggested that if leather be dissolved in sulphuric acid, its nitrogen will be made as available as that contained in the average animal matter. It is generally understood that many European manufacturers of fertilizers thus turn leather waste to account. No direct experiments are on record, so far as the writer is aware, to bear out the above claim.[2]

In order to study the value of dissolved leather, pot experi-

[1] Twelfth annual report of the Massachusetts Experiment Station, 1894. See also Agricultural Science, 8, Nos. 2 and 3.

[2] See however a single test reported in the Report of Connecticut Experiment Station for 1894, p. 101.

ments with oats were conducted during the years 1894 and 1895. The results obtained in 1894 have already been published.[1] The results for both years are presented below:

General Plan of the Experiment.—The experiments were conducted in galvanized iron pots. The soil, poor in all three ingredients of fertility, was supplied with an excess of potash and phosphoric acid. The nitrogen in sodium nitrate was taken as a standard, being rated at 100. The same quantity of nitrogen in sodium nitrate, Philadelphia tankage (roasted leather) and dissolved leather was applied to different sets of two or three pots each; one set of pots received no nitrogen. These latter pots measured the nitrogen capacity of the soil. The entire number of pots were treated as nearly alike as possible so far as sunlight, moisture, etc., were concerned. With similar conditions and plant food alike, excepting the nitrogen source, it is clear that the amount of nitrogen taken up by the plants in the different pots, would be a measure of the availability of the nitrogen in the several forms of nitrogen-containing material.

The Pots Used.—The pots, of thin galvanized iron, were seven and three-fourths inches in diameter and eight inches deep. A galvanized iron tube, half an inch in diameter, extended from the top to the bottom of the pot, connecting at the base with a second tube of the same material one inch in diameter. The latter tube extended along the bottom of the pot, and was perforated with small holes. The object of these tubes was to supply water partly from the bottom of the pot.

EXPERIMENTS A.

These experiments were begun in 1894 with eighteen pots, three parallel pots for each distinct test; they were continued in 1895 with twelve pots, two pots being employed for each test.

The Soil.—The soil was of a gravelly nature, and had not been cultivated for a long time. It was very poor in all three ingredients, as the following analysis will show:

	Per cent.
Water when tested	14.25
Phosphoric acid	0.13
Potassium oxide	0.08
Nitrogen	0.09

[1] *Loc. cit.*

Fertilizers Used.—The sources of nitrogen were sodium nitrate, Philadelphia tankage,[1] and dissolved leather. The dissolved leather was prepared in 1894 by heating 210 grams of C. P. sulphuric acid of 50° B. to 80° C. and slowly adding sixty-three grams of finely ground sole leather. The mixture was thoroughly stirred and allowed to stand one-half hour. A dark pasty mass resulted, to which were added forty-nine grams of water to thin somewhat, together with sufficient calcium carbonate to neutralize the excess of sulphuric acid, and to make the resulting mass suitable to handle. The calcium carbonate was used in preference to the phosphate, in our case, to avoid an excess of phosphoric acid. After standing twenty-four hours the mixture became dry and friable. The dissolved leather for 1895, was prepared in the same way, excepting that the water was omitted. Double superphosphate was used as a source of phosphoric acid, and potash was applied in the form of the double sulphate of magnesia and potash.

COMPOSITION OF FERTILIZERS USED.

	Nitrogen. Per cent.	Available phosphoric acid. Per cent.	Total phosphoric acid. Per cent.	Potassium oxide. Per cent.
Sodium nitrate for 1894 and 1895	14.28	....	....	....
Dissolved leather, I., 1894	0.97	....	....	....
" " I., 1895	0.97	....	....	....
Philadelphia tankage 1894 and 1895	7.80	....	....	....
Double superphosphate 1894 and 1895	....	47.42	47.80	
Double sulphate of magnesia and potash, 1894	....	....	....	24.32
Double sulphate of magnesia and potash, 1895	....	....	....	25.08

ARRANGEMENT OF THE EXPERIMENT.

1894.

Source of nitrogen.	Amount of nitrogen applied per pot. Gram.	Amount of available phosphoric acid applied per pot. Grams.	Amount of potassium oxide applied per pot. Grams.
Pots 1, 2, 3, soil nitrogen	0.00	1.20	2.40
" 7, 8, 9, sodium nitrate	0.30	1.20	2.40
" 13, 14, 15, dissolved leather	0.30	1.20	2.40
" 10, 11, 12, sodium nitrate	0.60	1.20	2.40
" 16, 17, 18, dissolved leather	0.60	1.20	2.40
" 4, 5, 6, Phil. tankage	0.60	1.20	2.40

[1] Roasted leather.

Pots 1, 4, 7, 10, 13, 16, were infected with a small quantity of cultivated soil, to note if the infection facilitated to any marked degree the nitrification of the organic nitrogen in case of these particular experiments. To each of these pots was also added ten grams of air-slaked lime.

1895.

Source of nitrogen.	Amount of nitrogen applied per pot. Grams.	Amount of available phosphoric acid per pot. Grams.	Amount of potassium oxide per pot. Grams.
Pots 1, 2, soil nitrogen	0.00	2.40	4.80
" 7, 8, sodium nitrate	0.30	2.40	4.80
" 13, 14, dissolved leather	0.30	2.40	4.80
" 10, 11, sodium nitrate	0.60	2.40	4,80
" 16, 17, dissolved leather	0.60	2.40	4.80
" 4, 5, Phil. tankage	0.60	2.40	4.80

It will be noticed that double the quantity of phosphoric acid and potash was applied in 1895, to make sure of a sufficient amount to enable the nitrogen to do its best work. To each of the pots was added ten grams of air-slaked lime. The same soil was used in 1895 as in 1894.

Filling the Pots.—About an inch of good clean gravel was first placed in the pots. All of the fertilizer excepting the nitrate was then mixed with eleven and one-half pounds of soil, which was put in in layers and gently pressed down. One-half gram of selected oats was then scattered over the soil, and covered with one pound of earth. The pots were thus filled to within one centimeter of the rim. One-half of the nitrate was applied in solution at the time of seeding, and the other half five to six weeks later.

General Care of the Pots.—The pots were set into a wagon running on an iron track. The floor of the wagon was surrounded with sides six inches deep. The pots were carefully watched and kept sufficiently watered. A portion of this water was supplied from beneath, and the remainder was added to the surface by the aid of a sprinkling pot. Sometimes it was necessary to water twice daily. The pots were kept in the open whenever the weather permitted. During wet or windy weather, and at night, they were run under cover.

Harvesting, etc.—The plants in pots 1, 2, 3, 4, 5, 6, in 1894, and in 1, 2, 4, 5, in 1895, were very light green and spindling during the entire growing period. The plants in the different pots were harvested as they matured. They were cut close to the soil, put in paper bags and hung away to dry. After the product of each pot was thoroughly air-dry, the grain was carefully removed, weighed, coarsely ground, and dry matter determinations made. The straw was cut into short lengths, and also tested for dry matter. Finally both grain and straw were ground fine, and nitrogen determinations made.

The figures in Tables I and II show the results obtained in two years. The first column in Table I shows the amount of nitrogen applied to each pot. The next four columns show the average dry matter produced for both years. The four columns next following indicate the gain in dry matter over soil nitrogen pots. The last column shows the average gain in dry matter of straw and grain for two years, produced by the different fertilizers, the gain produced by sodium nitrate being reckoned at 100.

It will be seen that the Philadelphia tankage has been but slightly available as a nitrogen source. Its effect the second year was rather better than during the first season. The combined results for the two years show it to be very inferior to the sodium nitrate, yielding practically one-tenth as much dry matter. These results simply confirm the investigations made by others with different forms of untreated leather.

The results with dissolved leather are very different. One could easily observe that during the entire growing season the plants treated with this substance were uniformly green, healthy, and grew continuously, being but little if any inferior in color to the sodium nitrate pots. The amount of dry matter obtained for two years with the aid of this source of nitrogen when compared with sodium nitrate, has been as 78 to 100.

The three-tenths gram of nitrogen from sodium nitrate the second year produced a poor yield of grain. This can only be accounted for from the fact that the second half of the nitrate was not applied until shortly before the grain began to head,

Table I.

	Nitrogen applied to each pot yearly.	Average dry matter produced.				Gain in dry matter over soil nitrogen pots, on basis of 0.3 gram of nitrogen applied.				If gain in dry matter with sodium nitrate = 100, then other sources of nitrogen would be equal to:				Average gain in straw and grain 1894 and 1895.
	Grams.	Straw. 1894 Grams.	Straw. 1895 Grams.	Grain. 1894 Grams.	Grain. 1895 Grams.	Straw. 1894 Grams.	Straw. 1895 Grams.	Grain. 1894 Grams.	Grain. 1895 Grams.	Straw. 1894	Straw. 1895	Grain. 1894	Grain. 1895	
Soil nitrogen........	0.000	7.82	8.64	1.69	1.32	....	....	....	....	....	....	....	....	....
Philadelphia tankage	0.600	8.88	11.10	1.66	2.66	0.53	1.23	±	0.67	5.40	13.75	±	31.45	7.5
Sodium nitrate......	0.300	17.59	17.59	6.37	3.45	9.77	8.95	4.68	2.13	100.00	100.00	100.00	100.00	100.00
Dissolved leather....	0.300	14.35	14.79	4.25	6.00	6.53	6.15	2.56	4.69	66.8	68.7	54.7	220.3	78.1
Sodium nitrate......	0.600	19.54	17.28	1.85	2.50	5.86	4.32	0.08	1.19	....	....	....	....	....
Dissolved leather....	0.600	19.76	19.76	4.92	5.15	5.97	5.56	1.61	1.91	....	....	....	....	....

Table II.

	Quantity nitrogen to each pot.	Nitrogen in total dry matter produced. Grams.			Average nitrogen in 100 grams dry matter. 1894 and 1895.		For every 100 parts of nitrogen applied there has been returned in straw and grain:		When sodium nitrate = 100 other sources of nitrogen equal to:	Every gram of nitrogen applied has produced in dry matter. Average 1894 and 1895.			For every 100 parts of straw, there has been produced in grain:
	Grams.	1894	1895	1894 and 1895	Straw. Grams.	Grain. Grams.	1894.	1895.	1894 and 1895.	Straw. Grams.	Grain. Grams.	Straw and Grain. Grams.	Grams.
Soil nitrogen.......	0.000	0.094	0.105	0.100	0.76	2.50	....	....	....	....	....	....	18.2
Phila. tankage......	0.600	0.126	0.163	0.144	0.94	2.39	5.3	9.67	11.00	2.49	1.12	3.61	38.1
Sodium nitrate.....	0.300	0.305	0.305	0.305	0.97	2.84	70.0	66.70	100.00	31.20	11.34	42.54	36.3
Dissolved leather...	0.300	0 210	0.273	0.241	0.71	2.70	39.0	56.00	70.00	21.13	12.07	33.20	57.2
Sodium nitrate.....	0.600	0.425	0.436	0.430	1.98	3.04	55.0	55.17	80.00	....	....	....	12.5
Dissolved leather...	0.600	0.325	0.374	0.349	1.00	2.99	39.0	44.83	62.00	....	....	....	31.7

and that this was not early enough for the plant to work it over into organic combination.

In cases where six-tenths of a gram of nitrogen was applied in the form of sodium nitrate but little grain was produced. This might be the result of two causes. First, because an excess of soluble nitrogen interfered with its natural transformation into organic combination, and in the next place it is possible, as already stated, that the second application was made too late. It is believed that the amount of phosphoric acid and potash applied especially the second year was in all cases sufficient. The six-tenths gram of nitrogen from the dissolved leather did rather better work than that from sodium nitrate, but it was still much inferior to that performed by three-tenths gram.

The amount of nitrogen obtained by the plant is a better measure of the availability of the nitrogen than the dry matter produced. This will be found in Table II. The first portion of the table shows the nitrogen in the total dry matter produced, and the average per cent. of nitrogen in 100 grams of dry matter. Next to be noted is the amount of nitrogen returned in the straw and grain, for every 100 parts of nitrogen applied. The results obtained from the several sources of nitrogen are then compared with the nitrogen obtained by the straw and grain of the sodium nitrate pots reckoned at 100. This comparison shows that the plants were able to take only about one-tenth as much nitrogen from Philadelphia tankage as from sodium nitrate, while they secured seven-tenths as much nitrogen from the dissolved leather as from the nitrate. When six-tenths gram of nitrogen was applied in the form of sodium nitrate and in dissolved leather, both the straw and grain contain a higher percentage of nitrogen than when but three-tenths gram was applied; the yield of straw and especially of grain was proportionately less, however, when the larger quantity was added. It is evident that a portion at least of the nitrogen taken up had not been turned to account in the production of organic substance.

EXPERIMENT B.

In this experiment, made in 1895, a soil was selected even poorer in nitrogen than the one used in Experiment A. The

object of this experiment was to see if more leather—than the amount used in the previous experiment—could not be added to the same quantity of stronger sulphuric acid, and thus secure a fertilizer testing higher in nitrogen. Dissolved leather II was therefore prepared by adding sixty grams of fine ground sole leather to 120 grams of 60° B. sulphuric acid heated to 200° F. The black pasty mass was allowed to stand for one-half hour, and was then dried off with calcium carbonate.

Dissolved leather III was prepared by adding 100 grams fine sole leather to 120 grams of 60° B. sulphuric acid. This amount of leather and acid—nearly one to one—furnished a very thick paste. It was dried off with calcium carbonate. The two dissolved leathers contained the following percentages of nitrogen:

	Per cent.
Dissolved leather II	1.13
" " III	1.75

The composition of the sulphate of potash and magnesia and of the double superphosphate, as well as the quantity applied, was the same as in Experiment A for 1895. The method of filling the pots, planting, and harvesting, was also similar.

Tables III and IV express the results in a similar way as Tables I and II. The sodium nitrate pots produced rather less grain than those to which the dissolved leather was applied. This tendency was noted in Experiment A. The three-tenths gram of nitrogen in the form of dissolved leather II produced about nine-tenths as much dry matter as did a like quantity of nitrogen in the form of sodium nitrate. The percentage of nitrogen in the dissolved leather plants is noticeably less however. The six-tenths gram of nitrogen from both the sodium nitrate and dissolved leather did not produce proportionately as much dry matter as did three-tenths gram, thus indicating that the plant was not able to work it all over into organic matter.

The three-tenths gram of nitrogen from dissolved leather III produced rather more dry matter than did the same quantity of nitrogen from sodium nitrate. The percentage of nitrogen in the straw and grain was decidedly less however.

Table IV shows that the oat plants were able to get but sixty-five per cent. as much nitrogen from dissolved leather II and III

TABLE III.

	Quantity of nitrogen to each pot.	Dry matter yielded by single pots.		Average dry matter from two pots.		Gain in dry matter over soil nitrogen pots on basis of 0.3 grams nitrogen applied.		If gain in dry matter with sodium nitrate=100, then other sources of nitrogen equal to:		Average Straw and Grain.
	Grams.	Straw. Grams.	Grain. Grams.	Straw. Grams.	Grain. Grams.	Straw. Grams.	Grain. Grams.	Straw. Grams.	Grain. Grams.	Grams.
Soil nitrogen	0.000 0.000	3.146 4.266	0.296 0.557	3.706	0.426	....	....	....	....	....
Sodium nitrate	0.300 0.300	12.104 13.286	3.057 4.557	12.695	3.807	8.989	3.381	100.00	100.00	100.00
Dissolved leather II...	0.300 0.300	11.122	4.417	11.122	4.117	7.416	3.691	82.5	109.00	89.8
Sodium nitrate	0.600 0.600	15.628 18.044	3.014 4.470	16.836	3.742	6.565	1.658	73.00	49.00	60.5
Dissolved leather II...	0.600 0.600	18.582 16.107	6.646 6.578	17.344	6.612	6.819	3.093	75.9	91.5	80.1
Dissolved leather III..	0.300 0.300	12.976 12.352	4.879 4.882	12.664	4.880	8.958	4.454	99.6	131.8	108.4

TABLE IV.

	Quantity of nitrogen to each pot.	Nitrogen yielded in total dry matter.	Nitrogen in 100 grams of dry matter.		For every 100 parts of nitrogen applied, there has been returned in straw as grain:	When sodium nitrate=100 other sources of nitrogen equal to:	For every gram of nitrogen applied there has been produced in dry matter:			For every 100 parts straw there has been produced in grain:
	Grams.	Grams.	Straw. Grams.	Grain. Grams.			Straw. Grams.	Grain. Grams.	Straw and Grain. Grams.	
Soil nitrogen	0.000	0.041	0.82	2.52	.....	....	....	....	....	11.5
Sodium nitrate	0.300	0.235	0.96	2.98	65.00	100.00	29.96	11.27	41.23	37.6
Dissolved leather II	0.300	0.165	0.66	2.06	41.00	63.1	24.72	13.30	38.02	49.8
Sodium nitrate	0.600	0.412	1.78	3.01	62.00	95.4	21.90	5.53	27.43	25.3
Dissolved leather II	0.600	0.305	0.83	2.43	42.00	65.0	22.73	10.31	33.04	45.4
Dissolved leather III	0.300	0.170	0.60	1.92	43.00	66.0	29.86	14.85	44.71	49.7

as from sodium nitrate. This confirms the results obtained in Experiment A for 1894. The oat plants secured twice as much nitrogen from the six-tenths gram as from the three-tenth gram in case of the sodium nitrate and both dissolved leathers, showing that the nitrogen was fully utilized.

GENERAL CONCLUSIONS.

The above experiments, part of which cover two years, make clear that dissolved leather, when properly prepared, yields as available a source of nitrogen as the average animal matter used for fertilizing purposes.

The quantity of nitrogen obtained by the plants from sodium nitrate being represented as equal to 100, the quantity obtained from dissolved leather during two years has been shown to be equal to 70.[1]

In this connection I beg leave to add the results of the availability of the various sources of nitrogen as determined by P. Wagner. Sodium nitrate is taken as 100 in value, and the value of other sources are compared with it.

Sodium nitrate	100
Ammonium sulphate	90
Dried blood, ground horn, and green plants	70
Ground bone, ground fish, and flesh	60
Stable manure	45
Ground wool	30
Ground leather	20

HATCH EXPERIMENT STATION,
AMHERST, MASS.

THE PROTEIDS OF THE POTATO.[2]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 21, 1896.

SO far as we can ascertain, the only investigations of the proteids obtained from the tubers of the potato have been made by Rüling,[3] Ritthausen,[4] Zöller,[5] and Vines.[6]

1 The Connecticut Experiment Station, in its recently issued report for 1895, confirmed these results.

2 From the report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

3 *Ann. Chem.* (Liebig), 58, 306.

4 Pflüger's Archiv, 21, 101.

5 *Ber. d. chem. Ges.*, 13, 1064.

6 *Journal of Physiology*, 3, 93.

Rüling contributes a partial analysis of the coagulum obtained by boiling the juice of the potato.

Ritthausen states that nearly the whole of the proteid of the potato is contained in the juice. He obtained two preparations from the juice by heating to 65° C., filtering off the coagulum and heating the filtrate to 76°. The two coagula were analyzed with results as stated beyond. He says, "these results do not contradict the assumption that the potato contains albumin, yet the content in sulphur is only one-half as great as in albumin of serum, egg and muscle.

Zöller extracted the pressed and washed potato pulp with ten per cent. sodium chloride brine and obtained a globulin, precipitable by saturating its solution with sodium chloride and when dissolved in ten per cent. sodium chloride brine coagulating on heating to 59° or 60°. From his result he concludes that the potato contains a globulin resembling myosin.

On investigating the juice of the potato Zöller obtained results which led him to conclude that the proteids therein dissolved are also globulins, but that further study was needed to explain their "peculiar deportment," especially, it is to be inferred, the fact of coagulation occurring at from 43° to 48°, and again, at 62°.

Vines states that prolonged treatment of the "crystalloids" of the potato with ten per cent. sodium chloride solution produces no apparent effect, but that they dissolve readily in a saturated solution of this salt, thus differing from all other protein crystals which he had observed.

Having had occasion to prepare a quantity of pure starch from the potato, we took advantage of the opportunity to examine the associated proteids.

After removing the skins, the tubers were crushed and squeezed in a drug press. The juice was strained through cloth and allowed to stand and deposit the greater part of the suspended matters. It was then saturated with ammonium sulphate and the precipitate so produced was filtered out. The potato pulp was washed with water and the washings after clearing were also saturated with ammonium sulphate. The

two precipitates thus obtained were united, dissolved in salt solution, filtered clear and dialyzed.

The washed pulp was then treated with ten per cent. sodium chloride solution; the proteid, thus extracted, was precipitated with ammonium sulphate, dissolved in salt solution, filtered clear, and also dialyzed. The globulin precipitated very slowly on dialysis, and after fourteen days was filtered out. The proteid obtained from the juice was much greater in amount than that from the salt extract of the pulp. The globulin, from both juice and salt extract, was then dissolved in salt solution, the solutions were united, filtered from a considerable quantity of insoluble globulin (rendered insoluble by long contact with water), and the solution again dialyzed. After freeing from chlorides, the contents of the dialyzer were filtered, the reprecipitated globulin was washed with water and alcohol and dried over sulphuric acid, giving preparation 1, weighing 7.34 grams.

The filtrate, from preparation 1, still contained proteid and was therefore saturated with sodium chloride, which completely precipitated the remaining globulin. This was then dissolved in dilute salt solution and dialyzed in water until free from chlorides and, as the proteid was not thus precipitated, the dialyzer was transferred to alcohol, which soon threw down all the proteid. This was filtered out, washed in water and absolute alcohol and dried, giving one-half gram of preparation 2.

The solutions, filtered from the globulin precipitated by the dialysis first described, were united and, in order to obtain the proteid in a solution of smaller volume, the liquid was saturated with ammonium sulphate, the precipitate produced was dissolved in a little water and the clear solution dialyzed, first in river water and then in distilled water. The globulin so precipitated was filtered out, washed with water and absolute alcohol and dried, yielding preparation 3, weighing 3.40 grams. The filtrate from this preparation was dialyzed into alcohol and the resulting precipitate filtered out, washed with absolute alcohol, and dried, forming preparation 4, which weighed 1.74 grams.

The filtrate from 4 was further dialyzed in alcohol and the proteid completely precipitated by adding absolute alcohol. This substance, after filtering out, washing with absolute alco-

hol and drying, weighed 0.53 gram and formed preparation 5.

These several preparations were analyzed after drying them at 110°, with the following results:

POTATO GLOBULIN. TUBERIN.

	Osborne and Campbell.					Ritthausen.	
	1.	2.	3.	4.	5.	I.	II.
Carbon	53.62	....	53.58	53.64	....	....	53.87
Hydrogen	6.80	....	6.91	6.83	....	....	7.30
Nitrogen	16.15	16.29	16.36	16.34	16.07	15.76	15.98
Sulphur	1.22	....	1.27	23.19	....	....	0.86
Oxygen	22.21	....	21.88				21.99
	100.00		100.00	100.00			100.00

The close agreement in composition among our five fractions is in itself, strong evidence that, besides this globulin, but little proteid is present in the potato. These five fractions practically include the whole of the proteid matter dissolved in the juice and salt extracts. The above figures given by Ritthausen for the composition of the proteid, obtained by coagulation of the juice at 65° and 76°, are also in close agreement with ours, excepting those for sulphur. The slightly lower nitrogen content of the coagulated globulin is to be expected, since proteids generally, if not always, yield some ammonia when coagulated by heat.

The potato globulin, when heated slowly in a double water-bath, shows a wide range of variation in its coagulation point depending on the conditions under which it is dissolved.

A solution of this globulin prepared by treating a portion of preparation 1 with ten per cent. sodium chloride solution and filtering out the insoluble matter, became turbid at 56° and a flocculent coagulum separated at 64°. After heating some time at 70° the coagulum was filtered out and the filtrate, when again tested, gave a turbidity at 72° and a flocculent coagulum at 76°.

Another preparation of this globulin was extracted, in the same way, with ten per cent. salt solution, and the dissolved proteid was filtered from the insoluble matter and precipitated by saturating the solution with sodium chloride. The precipitated globulin was washed with saturated salt solution and removed from the paper mixed with a considerable quantity of the concentrated brine. Distilled water was gradually added

until all of the proteid dissolved. The resulting solution was therefore almost completely saturated with the proteid. This solution, when slowly heated in the double water-bath to 44° C., and held at this temperature some minutes, became turbid and after a time flocculent, although the temperature remained perfectly constant. After raising the temperature to 50° it was filtered from the small coagulum which had formed and again heated, turbidity occurring at 50½° and flocks separating at 51°. After heating some time at 56° the solution was filtered from the second small coagulum and again tested. Turbidity occurred at 58° and flocks separated at 59°, gradually increasing to a large coagulum at 66°, which was filtered out. The filtrate now became turbid at 63°, flocks forming at 66°, and increasing to a considerable coagulum at 70°. The temperature was raised to 80° and the coagulum, which was about the same in amount as that formed at 66°, was filtered out. The filtrate gave only a trace of coagulum on boiling. The two coagula first formed were very small compared with the last two.

This test was then repeated with the same solution diluted with an equal volume of water. This solution was heated for some time at 44°, but remained perfectly clear. The temperature was then very slowly increased and at 53° a turbidity formed which, however, was scarcely greater at 56°. Above this temperature the turbidity increased until flocks separated at 62°, and a large coagulum formed at 65°. The solution filtered at 66°, gave a turbidity at 66°, with flocks at 68°, which formed a large coagulum on gradually raising the temperature to 80°, the filtrate from which gave no more coagulum on boiling.

The test was again repeated by mixing four parts of the same solution with one of water, and the same results obtained as with the solution diluted with an equal volume of water. This shows that within wide limits the temperature of coagulation does not depend on the relative quantity of dissolved proteid, but that the very low coagulation point of the undiluted solution was probably due to the presence of nearly enough sodium chloride to cause precipitation of the globulin. It will be noticed that coagulation of the proteid, which began at 56°, was not completed until the temperature had reached at about 80°.

This does not necessarily show the presence of several proteids, for such gradual coagulation is characteristic of most plant globulins, many being only very slowly coagulated, even by long boiling.[1] The coagulum separated by heating solutions of this globulin to 75° C. is very soluble, on gently warming, in extremely dilute hydrochloric acid, even acid of 0.01 per cent. dissolving the substance readily at 40°–50° C. The coagulum dissolves quickly and completely in one-tenth per cent. caustic potash solution at 20° and in one per cent. sodium carbonate solution at 70° C. These solutions are precipitated by neutralization, but the substance thrown down is not soluble in salt solutions. The low heat-coagulation point obtained for the solution of the globulin precipitated with salt and dissolved in a minimum quantity of water is in accord with that given by Zöller for the proteid similarly obtained by him from the juice of the potato, and our observations explain to some extent the questions which he considered to require further investigation.

In order to determine more definitely whether other proteids were present with the globulin, a larger quantity of filtered potato juice, obtained from potatoes which had been washed carefully, but from which the skins had not been removed, was saturated with ammonium sulphate, the precipitate was dissolved in dilute salt solution, which was then filtered and saturated with sodium chloride. The globulin thus precipitated was filtered out, the filtrate was dialyzed for twenty-four hours in order to remove a considerable part of the salt, and was then saturated with ammonium sulphate. The small quantity of proteid thus precipitated was filtered out, dissolved in a little dilute salt solution and sodium chloride added to complete saturation. A considerable part of the dissolved proteid was thereby precipitated, which was filtered out and dissolved in dilute salt solution. The resulting liquid became turbid on heating to 58° C. and flocculent at 60°. The substance was evidently a part of the globulin which had escaped precipitation on the first saturation with salt, probably owing to the presence of some constituent of the juice.

The solution filtered from the salt saturation precipitate *last*

1 Chittenden and Mendel, *Journal of Physiology*, 17, 52.

described, was diluted with two volumes of water and then saturated with ammonium sulphate. The proteid thus separated was filtered out, dissolved in water, and found to yield a turbidity at 52° and a flocculent coagulum at 58°, a coagulation point not essentially differing from that of the globulin.

The whole solution was then heated for some time at 70° C. in a water-bath, the coagulum which separated was filtered out, and the filtrate, after removing a small quantity of coagulum, which separated on heating to 75°, was boiled and found to remain clear. This solution was then saturated with ammonium sulphate and the very small precipitate produced was filtered out, dissolved in a small amount of water and tested with the following results: nitric acid added to the solution in the cold gave no precipitate; saturation with sodium chloride gave no precipitate even when acetic acid was added. The biuret test was without result owing to the strong brown color of the solution. This substance therefore failed to give the most characteristic reactions of the proteoses, yet it must be considered as a proteose since in its essential properties it agrees more closely with this class of proteids than with any other.

The experiments made by Zöller on the juice of the potato were repeated by us with the same results as described by him, except that we found the solution of the precipitate produced by saturation with salt, to yield a flocculent coagulum at 52°, while Zöller's solution coagulated at 46°–48°. It has already been shown that a solution of the globulin similarly prepared gave a coagulum at 44°, and on dilution with one volume, as well as with one-fourth volume of water, the same solution coagulated at 62°. It is thus evident that the temperature of coagulation is not to be depended upon as a means of identifying this proteid with certainty. The other reactions described by Zöller are those given by the potato globulin. From these results then it would appear that by saturating the juice of the potato with sodium chloride the greater part of the globulin is precipitated, but that a not inconsiderable part remains in solution. If this is separated by saturation with ammonium sulphate and the precipitate so produced is dissolved in water, a large part of this globulin can be precipitated by again saturating with salt. The

proteid still remaining in solution is nearly all coagulable and the solution on heating behaves exactly like a solution of the globulin.

CONCLUSION.

The proteids of the potato tuber consist of a globulin, for which we propose the name *Tuberin*, and a proteose, the latter occurring in very small amount. The properties of tuberin were found to be as follows:

It is precipitated by saturating its solutions with sodium chloride, sodium sulphate, magnesium sulphate, or ammonium sulphate. By acetic acid or nitric acid a precipitate is given readily soluble in an excess of acid even in the presence of salts. Potassium ferrocyanide gives no precipitate until acetic acid is added. Mercuric chloride gives no precipitate, but picric acid or tannic acid throw down the globulin. With the biuret, Millon's and the xanthoproteic tests the usual reactions are given.

Tuberin is soluble in very dilute saline solutions and therefore the juice of the potato contains the greater part of this proteid. By dialysis it is precipitated slowly and incompletely because of the difficulty of removing *all* soluble salts by this process. Like other easily soluble globulins it readily changes to the insoluble modifications, so that preparations made by dialysis are to a great extent insoluble in saline solutions. In contact with alcohol it very quickly loses its solubility.

When dissolved in ten per cent. sodium chloride solution tuberin shows a somewhat variable heat-coagulation point depending on the conditions under which it is tested. In general a flocculent coagulum is formed on heating to 60°–65° C. Coagulation is, however, not complete until the solutions have been heated for some time at 80° C. The composition of this globulin was found from an average of several accordant analyses to be:

TUBERIN.

Carbon	53.61
Hydrogen	6.85
Nitrogen	16.24
Sulphur	1.25
Oxygen	22.05
	100.00

LEGUMIN AND OTHER PROTEIDS OF THE PEA AND THE VETCH.[1]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 21, 1896.

LEGUMIN.

UNDER the name Legumin, many preparations, obtained from various seeds, have been described, but in such different and often conflicting terms as to leave us completely in doubt with regard to the nature of this substance.

This confusion appears to have arisen largely through the mistaken idea, which formerly was very generally held, that all the proteids extracted from seeds by water and precipitated by acids are one and the same substance.

The methods of analysis employed by the earlier chemists were too crude or uncertain to set forth the slight differences in composition of the various plant proteids, and the difficulty of making pure preparations tended, as the subject was further studied, to add to the confusion. Since the methods of analysis have been perfected and the more recently developed modes of studying proteids introduced, legumin has received little or no attention. In recent literature legumin is most commonly referred to as a substance extracted from seeds by caustic alkalies, and more or less altered by the action of the solvent, but nothing has been done, to our knowledge, to show the nature of the original proteid.

The object of our investigation has been to examine the seeds in which legumin is said to exist and to determine as definitely as possible the composition and character of this substance.

In 1806 Einhof[2] recognized a proteid in beans and lentils which he considered to be different from the bodies of this class previously known.

Braconnot[3] named this substance legumin.

Noad[4] prepared and analyzed legumin from peas and beans.

Norton[5] prepared legumin from peas, sweet almonds, and oats, and gave analysis of his preparations.

1 From the Report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

2 Gehlens: *J. d. Chem.*, 6, 543.

3 *Ann. de Chim. et de Phys.*, 34, [2] 68, *1827*.

4 *Chem. Gaz.*, *1847*, 357.

5 *Am. J. Sci.*, [2], 5, 22, *1847*.

Loewenberg[1] considered that legumin, as previously prepared, contained albumin and devised a method for the separation of these two proteids and gave analyses of the substances so prepared from almonds and peas.

Liebig[2] obtained plant casein (legumin) from beans, lentils, and peas, and gave an account of the properties of this proteid and two analyses. He concluded that the substance was identical in properties and composition with milk casein.

Dumas and Cahours[3] prepared legumin from peas, lentils, beans, almonds, plums, filberts, and white mustard. They considered all these seeds to contain the some proteid substance; that obtained from the three first named seeds being less pure than that from the others and therefore containing somewhat less nitrogen.

They gave analyses of preparations from all these seeds and an extended account of the properties of legumin, based on a study of the preparation obtained from the almond.

Contrary to Liebig, they concluded that this substance is not identical either with milk casein or plant casein. The latter designation they applied to the body which separates out on cooling a concentrated hot alcoholic extract of wheat gluten.

Rochleder[4] pointed out that the substance obtained from beans, lentils, and peas by Liebig was different from that of the almond described by Dumas and Cahours, and that for this reason these investigators did not reach the same conclusions. Rochleder prepared and analyzed legumin from two varieties of beans.

In 1868 Ritthausen undertook a study of legumin, the results of which are recorded in a series of papers whose publication extended over a period of fifteen years.[5]

He recognized that the seeds of almonds, plums, filberts, and white mustard, which had been previously stated to yield legumin, really contain a different proteid, which he called *conglutin*.

1 *Ann. Phys.*, Pogg., **78**, 327.

2 *Ann. d. Chem. u. Pharm.*, **39**, 138.

3 *J. prakt. Chem.*, **28**, 398.

4 *Ann. d. Chem. u. Pharm.*, **46**, 155.

5 *J. prakt. Chem.*, **103**, 65, *1868*: Die Eiweisskörper, etc., Bonn., *1872*: Pflüger's Archiv., **15**, 269, *1877*: *Ibid*, **16**, 293, *1878*: *Ibid*, **18**, 236, *1781*; *J. prakt. Chem.*, [2], **24**, 221, *1881*; *Ibid*, [2], **26**, 504, *1882*.

Up to this time legumin was considered to be the proteid that is extracted from seeds with water and is precipitated by acids from the aqueous extract.

All proteids thus obtained had been regarded as identical by most investigators and were known either as legumin or plant casein. Although it had been suggested that different seeds yield different proteids, Ritthausen appears to have been the first to make this fact evident. Ritthausen prepared "legumin" from blue lupins, yellow, green, and gray field peas, yellow garden peas, lentils, vetches, horse beans (Vicia faba), white and yellow beans (Phaseolus) and colza cake. The proteid of Phaseolus, Ritthausen afterwards found to be distinct from legumin, and one of us has, in the main, confirmed his later result and has named the proteid phaseolin.[1] Ritthausen afterwards considered the proteid which he obtained from colza cake to be an impure preparation of a different substance. His early analyses[2] of preparations from the leguminous seeds were fairly accordant, but he afterwards found that the soda lime method which was used in determining nitrogen gave too low results. He thereupon determined nitrogen anew by Dumas' method, and published a revised statement of the mean composition of legumin.[3]

In another paper published shortly afterwards, Ritthausen withdrew the corrected figures for nitrogen, having found that they were too high, because the nitrogen of his later analyses was mixed with hydrogen. He therefore published a third set of figures for nitrogen and made a second revised statement of the mean composion of legumin.[4]

At this time Hoppe-Seyler[5] and Th. Weyl[6] stated that the proteids of plants are chiefly globulins and Weyl examined qualitatively a number of seeds, by extracting then with ten per cent. sodium chloride solution, and found proteids resembling in their reactions animal myosin and vitellin. They asserted

1 Report of the Conn. Agricultural Experiment Station, 1893, p. 186. and This Journal, 16, 633.

2 Die Eiweisskörper, etc., Bonn., 1872. pp. 159, 176.

3 Pflüger, Archiv., 16, 293, *1877*.

4 Pflüger, Archiv., 18, 236. *1878*.

5 *Physiol. Chemie.*, p. 75.

6 *Ztschr. phys. Chem.*, 1, 72.

that the substance called legumin by Ritthausen was doubtless originally a globulin and that the preparations of this substance described and analyzed by him were altered by the alkali which he used in extracting them and were not the proteids originally contained in the seeds. Ritthausen contended strongly against this view and maintained that his preparations were wholly unaltered by the alkali. He extracted several kinds of seeds with salt solution, precipitated the proteid by dilution with water and found that the preparations of legumin so made were not essentially different in composition from those obtained by extracting with dilute potash water.[1] He then examined his older preparations, made by extracting the seeds with weak alkali and showed that they were to a very considerable extent soluble in salt solution. The substance thus extracted had, in many cases, a different composition from that of the original preparation, and Ritthausen then concluded that all the preparations which he had previously described as legumin were, in fact, mixtures of the two proteids, one, soluble in salt solution after dissolving in potash water and precipitating with acid, similar to, but distinct from conglutin, and the other originally soluble in salt solution but rendered insoluble in that fluid by treatment with alkalies. This latter he called legumin.

He then purified the legumin by extracting the mixed proteids from the seed with dilute alkali, neutralizing with acid, extracting the precipitate so produced with sodium chloride solution to remove proteids soluble in that fluid and then redissolving the residue, consisting mostly of legumin, in dilute alkali and reprecipitating with acetic acid.

Two preparations were so obtained, one from the pea and another from the horse bean (*Vicia faba*).

Ritthausen regarded his study of these preparations as showing that the substance from *Vicia faba* was a compound of tannic acid with the salt soluble proteid and that it was doubtful whether the horse bean contains legumin at all.

The preparation from the pea he finally considered to be legumin, having the following composition :

[1] *J. prakt. Chem.*, 26, 504.

LEGUMIN OF PEA, RITTHAUSEN.

Carbon	51.34
Hydrogen	6.98
Nitrogen	17.48
Sulphur	0.45
Oxygen	22.75
	100.00

This analysis represents the composition of legumin not in its original condition, but so altered as to be insoluble in saline solutions. Of the reactions of legumin we know little more than that it dissolves in salt solution and is precipitated by diluting with water.

In the following pages we give the outcome of our recent investigation into the composition and properties of legumin as contained in the seeds of the pea and the vetch.

Here, as in former papers, we have described our procedure with considerable, perhaps unnecessary, detail, but having often experienced great difficulty in understanding and repeating the work of our predecessors because of the vagueness of their statements, we have endeavored to describe our methods and results so fully and accurately that any who may wish to review our investigations experimentally may find it practicable to do so.

I. PROTEIDS OF THE PEA.

One hundred grams of garden peas ground to pass a sieve of one mm. mesh were extracted with petroleum naphtha to remove oil, then dried by exposure to the air, and finally treated with one liter of ten per cent. sodium chloride solution. As the very viscid extract could scarcely be filtered through paper, an equal volume of ten per cent. sodium chloride solution was added, and after some time one-half the solution passed the filter clear. This was saturated with ammonium sulphate, the resulting precipitate was filtered out, dissolved in salt solution, and the liquid dialyzed free from chlorides. The proteid separated, as do all vegetable globulins thus far observed, in spheroids. No distinct crystals could be detected in this or any of our preparations from the pea. When the chloride had been removed by dialysis the precipitate was filtered out, washed with water and alcohol, dried over sulphuric acid, and found to weigh three

and a half grams, being about seven per cent. of the meal. Dried at 110° this preparation was analyzed with the following results:

PEA LEGUMIN, 1.

Carbon	52.03
Hydrogen	6.96
Nitrogen	17.98
Sulphur } Oxygen	23.03
	100.00
Ash	0.41

Another preparation was made by extracting 500 grams of pea meal with three liters of ten per cent. sodium chloride brine and after allowing the mixture, protected with thymol, to stand three days in a cool place, 1500 cc. of the extract were decanted. Although very turbid, this was saturated with ammonium sulphate without filtering, and the precipitate produced was filtered out and dissolved in brine. The resulting solution was then filtered without much trouble and the clear filtrate dialyzed free from chlorides. After washing and drying the globulin thus precipitated, and amounting to ten grams or about five per cent. of the meal, had the following composition:

PEA LEGUMIN, 2.

	I.	II.	Average.
Carbon	52.08	52.19	52.14
Hydrogen	7.06	6.95	7.01
Nitrogen	18.01	17.91	17.96
Sulphur	0.49	....	0.49
Oxygen	....	....	22.40
			100.00
Ash	0.33		

In order to obtain larger quantities of this proteid for fractional precipitations 800 grams of pea meal were treated with four liters of *twenty* per cent. sodium chloride solution, and by draining on filters over night about one-half the solution applied to the meal, or two liters, was obtained as a clear yellow filtrate, which was saturated with ammonium sulphate, but for a reason, then unknown, very little proteid separated. Dilute acetic acid saturated with ammonium sulphate was then added in small

amount and the proteid separated as a flocculent precipitate. This was filtered out and in order to remove the acid as completely as possible the precipitate was suspended in about four liters of saturated ammonium sulphate solution and again filtered out. The precipitate was then dissolved in ten per cent. sodium chloride solution and calcium carbonate added to neutralize the acid retained by the proteid. The solution then reacted alkaline with litmus owing to ammonium carbonate set free from the sulphate. The solution was next filtered very nearly clear and dialyzed until a large precipitate had formed. This precipitate was filtered out, dissolved in salt solution, filtered clear and dialyzed free from chlorides. The precipitated globulin was washed with water and alcohol and dried over sulphuric acid, giving fifty-two grams, in whose analysis, after drying at 110°, the following figures were obtained:

PEA LEGUMIN, 3.

	I.	II.	Average.
Carbon	52.30	52.27	52.29
Hydrogen	7.06	6.98	7.02
Nitrogen	17.72	17.79	17.76
Sulphur	0.30	....	0.30
Oxygen	....	....	22.63
			100.00
Ash	0.53		

The solution filtered from this substance after its first precipitation by dialysis was saturated with ammonium sulphate, the resulting precipitate filtered out and dissolved in a little water, filtered clear and dialyzed. After removing the greater part of the salts by dialysis the precipitated globulin was filtered out, treated in the usual manner, and gave 14.2 grams of preparation 4, having, when dried at 110°, the following composition:

PEA PROTEID, 4.

	I.	II.	Average.
Carbon	52.50	....	52.50
Hydrogen	6.74	....	6.74
Nitrogen	16.83	16.76	16.80
Sulphur	0.49	....	0.49
Oxygen	....	....	23.73
			100.00
Ash	0.33		

Preparation 3, when dissolved in ten per cent. salt solution, was found to become turbid at 97° and after long heating in a boiling water-bath slowly developed a coagulum. Preparation 4 contained a considerable quantity of proteid coagulating at a much lower temperature. It was accordingly dissolved, as far as possible, in a little ten per cent. salt solution and the insoluble matter filtered out. The clear filtrate was diluted with distilled water until the solution contained 0.66 per cent. of salt, when a not inconsiderable precipitate formed, which was filtered out and the filtrate saturated with ammonium sulphate. This produced a relatively abundant precipitate, which was filtered out and dissolved in water. This solution, on heating, became turbid at 52°, and on keeping for some time at this temperature a minute quantity of flocks separated. Filtered at 56°, turbidity occurred again at 62° and a few flocks formed at 66°. Filtered at 67°, the solution became turbid at 70°, the turbidity increasing above 75° to a heavy flocculent coagulum at 79°.

It is evident from these results that we have in preparation 4 at least two proteids, one coagulating at 79°, the other being only slowly and imperfectly coagulated at 99°–100°; the former is readily soluble in very dilute salt solutions, the latter only slightly soluble in solutions containing less than one per cent. of salt. The filtrate from preparation 4 was dialyzed in water, but as no more globulin separated, the dialyzer was transferred to alcohol and the proteid thus completely thrown down. After washing with absolute alcohol and drying over sulphuric acid 12.31 grams of substance were obtained. This, of course, was a mixture of all the proteids extracted from the pea which had not been precipitated by dialysis in water. It was therefore treated with two per cent. salt solution, a large quantity of proteid which had been coagulated by the alcohol was filtered out, washed with water, with dilute and absolute alcohol, and dried over sulphuric acid. This preparation, 5, weighed 7.45 grams, and gave the following results when analyzed, after drying at 110°.

PEA PROTEID, 5.

	I.	II.	Average.
Carbon	53.40	53.26	53.33
Hydrogen	6.92	7.03	6.98
Nitrogen	16.19	16.09	16.14
Sulphur	1.00	....	1.00
Oxygen	....	....	22.55
			100.00
Ash			0.32

The filtrate from 5 was saturated with ammonium sulphate, whereupon a small gummy precipitate appeared which was filtered out and dissolved in a small quantity of water. This solution when heated became turbid at 49° and flocculent at 60°; filtered at 75°, turbidity occurred on heating again to 72° and flocks formed at 79°. After heating to about 90° no more proteid was coagulated by boiling. The solution now contained a very small quantity of proteose.

Since acetic acid was used to separate the substance, from which 3, 4 and 5 were obtained, from the ammonium sulphate solution, it was necessary to obtain more of the proteids without the use of acid. It was found that the incomplete precipitation by ammonium sulphate was due to the use of twenty per cent. sodium chloride solution, in which less ammonium sulphate dissolves than in a ten per cent, salt solution, not enough, in fact, to completely precipitate the proteid. The meal residue was therefore treated with water enough to reduce the strength of the salt solution still adhering to it to about ten per cent. A further considerable quantity of nearly clear extract was thus obtained, which, when saturated with ammonium sulphate, readily and completely parted with the proteid. This was filtered out, dissolved in ten per cent. brine, the solution filtered perfectly clear and dialyzed. After a large quantity of globulin had separated in the dialyzer its contents were filtered off, the precipitate was dissolved in ten per cent. salt solution and treated in exactly the same way as 3 had been. This preparation, 6, weighed 37.5 grams and, dried at 110°, had the following composition :

PEA LEGUMIN, 6.

	I.	II.	Average.
Carbon	52.37	....	52.37
Hydrogen	6.90	....	6.90
Nitrogen	17.95	17.95	17.95
Sulphur	0.39	....	0.39
Oxygen	....	....	22.39
			100.00
Ash	0.28		

The filtrate from the first precipitation, by dialysis, of this substance, when saturated with ammonium sulphate gave a precipitate which was dissolved in a little water and the resulting solution was filtered clear and dialyzed. After most of the salts were thus removed the separated globulin was filtered out, washed and dried, and gave 2.44 grams of preparation 7, having the following composition, when dried at 110°:

PEA PROTEID, 7.

	I.	II.	Average.
Carbon	52.09	52.02	52.06
Hydrogen	6.96	7.08	7.02
Nitrogen	16.75	16.57	16.66
Sulphur	0.55	....	0.55
Oxygen	....	....	23.71
			100.00
Ash	0.20		

This analysis is in fair accord with that of the similarly obtained preparation 4.

The filtrate from 7 was dialyzed into alcohol and then absolute alcohol was added to the solution until all the proteids separated. The precipitate thus produced was filtered out, washed with absolute alcohol, dried over sulphuric acid and found to weigh 7.1 grams. Since this preparation might be a mixture of any unprecipitated globulin, with albumin and proteose, if these were present, it was treated with water and the considerable quantity of proteid coagulated by alcohol was filtered out, washed thoroughly with water and then with absolute alcohol and dried over sulphuric acid. This gave 4.05 grams of preparation 8, which, when dried at 110°, had the following composition:

PEA PROTEID, 8.

	I.	II.	Average.
Carbon	53.60	53.47	53.54
Hydrogen	6.99	6.98	6.99
Nitrogen	16.72	16.65	16.69
Sulphur	1.01	....	1.01
Oxygen	....	....	21.77
			100.00
Ash	0.32		

The analysis of 8 agrees well with that of 5 and it is probable that these figures pretty nearly represent the composition of a second proteid (globulin or albumin) readily soluble in very dilute salt solutions.

Having thus found evidence of the presence of at least two proteids in the pea extract, one less soluble than the other in very dilute salt solutions, it became necessary to subject the less soluble and more abundant globulin to thorough fractioning in order to learn whether it was homogeneous or a mixture.

Twenty-five grams of 3 were therefore dissolved in 250 cc. of five per cent. sodium chloride solution, filtered clear and the filter washed with fifty cc. of the same salt solution. A portion of the preparation had, as is usually the case with vegetable globulins when dried, passed into an insoluble form. This insoluble matter when treated with salt solution gave a gummy residue, which was difficult to filter out. No estimate of the amount of this substance could be made.

The clear salt solution of the globulin was diluted with twice its volume of water, making 750 cc. of a 1.67 per cent. solution of sodium chloride. After standing over night the proteid which had precipitated on dilution was collected on a filter, washed with water and alcohol and dried over sulphuric acid. Preparation 9 was so obtained, weighing five and one tenth grams and having, when dried at 110°, the composition given below.

The solution filtered from this substance was treated with an equal volume of water making 1500 cc. of a brine containing 0.84 per cent. of salt, from which after standing some time a part of the proteid separated as a viscid layer at the bottom of the beaker. The solution was decanted and the precipitate

washed and dried in the usual manner. This, 10, weighed 5.29 grams. The decanted liquid was then dialyzed free from salt and the precipitated globulin treated in the usual manner, giving 11, weighing 4.10 grams. About three-fifths of the original substance was thus recovered in three nearly equal fractions. The other two-fifths consisted largely of insoluble globulin. The composition of the fractions so obtained was as follows:

PEA LEGUMIN, FRACTIONS OF 3.

	9.			10.			11.		
	I.	II.	Average.	I.	II.	Average.	I.	II.	Average.
Carbon	52.49	52.23	52.36	52.31	52.09	52.20	52.25	52.25	52.25
Hydrogen	7.11	7.10	7.11	7.09	6.92	7.01	7.08	....	7.08
Nitrogen	17.96	18.05	18.01	17.98	17.96	17.97	17.88	17.84	17.86
Sulphur	0.35	....	0.35	0.35	....	0.35	....	....	22.81
Oxygen	....	....	22.17		....	22.47	....	....	
			100.00			100.00			100.00
Ash			0.22			0.61			0.20

Again, twenty-five grams of preparation 6 were dissolved in 250 cc. of five per cent. brine, the solution filtered, the residue washed with fifty cc. of the same brine and the clear filtrate diluted with one and a half volumes of water, thus giving a two per cent. salt solution. After standing over night the precipitate was filtered out, washed with water and alcohol and dried over sulphuric acid. Preparation 12 so obtained weighed 8.58 grams.

The filtrate from 12, on adding an equal volume of water and treating the precipitate as just described, yielded 13, weighing 2.84 grams.

The filtrate from 13, dialyzed free from salt, gave 14, weighing four and two tenths grams.

PEA LEGUMIN, FRACTIONS OF 6.

	12.			13.	14.		
	I.	II.	Average.		I.	II.	Average.
Carbon	52.26	....	52.26	52.08	52.01	52.02	52.02
Hydrogen	6.96	....	6.96	7.04	....	7.20	7.20
Nitrogen	17.96	18.06	18.01	17.88	17.81	18.03	17.92
Sulphur	0.44	....	0.44	23.00	....	....	23.86
Oxygen	....	....	22.33		....	....	
			100.00	100.00			100.00
Ash			0.40	0.19			0.17

Comparing the analyses of these fractions with each other and with that of the original substance, it is plain that they all represent a single proteid.

SUMMARY OF ANALYSES OF PEA LEGUMIN.

	1.	2.	3.	6.	9.	10.	11.
Carbon	52.03	52.14	52.29	52.37	52.36	52.20	52.25
Hydrogen	6.96	7.01	7.02	6.90	7.11	7.01	7.08
Nitrogen	17.98	17.96	17.76	17.95	18.01	17.97	17.86
Sulphur	23.03	0.49	0.30	0.39	0.35	0.35	22.81
Oxygen		22.40	22.63	22.39	22.17	22.47	
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	12.	13.	14.	Average.
Carbon	52.26	52.08	52.02	52.20
Hydrogen	6.96	7.04	7.20	7.03
Nitrogen	18.01	17.88	17.92	17.93
Sulphur	0.44	23.00	22.86	22.45
Oxygen	22.33			
	100.00	100.00	100.00	100.00

Ritthausen obtained from peas by extraction with salt solution and precipitation with water two preparations, the analyses of which are given below, A and B.[1]

By treating peas with very weak potash water, adding acid to neutralization, extracting the precipitate thus produced with salt solution and filtering out the insoluble matter, he obtained a solution from which, by adding water, a precipitate was thrown down whose composition is given below under C.

PEA LEGUMIN.

	Ritthausen. A.	B.	C.	Osborne & Campbell. Average of 18 analyses on 10 preparations.
Carbon	52.83	51.61	51.62	52.20
Hydrogen	7.27	7.08	6.96	7.03
Nitrogen	17.26	17.23	18.26	17.90
Sulphur	22.64	24.08	0.33	0.39
Oxygen			22.83	22.48
	100.00	100.00	100.00	100.00

Ritthausen's preparation C agrees fairly well with the average of our results. The preparations extracted directly from peas

[1] *J. prakt. Chem.*, 26, 504.

by salt solution would appear to be the same substance but less pure. We see no ground for Ritthausen's idea that his older preparations were mixtures of two proteids both originally soluble in salt solution, one of which, legumin, is rendered insoluble in salt solution by treatment with alkalies. It is much more probable that a part of the globulin in his preparations had assumed the insoluble condition during the process of separating since nearly all globulins, to a greater or less extent, are prone to this change. The difference in composition between Ritthausen's original "legumin" and the substance extracted from it by salt solution is doubtless due to the greater purity of the latter. This view is supported by the close agreement in composition of this substance with those extracted by us directly from the pea. For this, the chief proteid of the pea, it is proper to retain the name *Legumin* first proposed by Braconnot.

The properties of legumin are as follows:

In water it is entirely insoluble.

In ten per cent. sodium chloride solution, when freshly prepared and not dried, it is readily soluble, but after washing with alcohol and drying over sulphuric acid, more or less becomes insoluble in salt solution. Dissolved in ten per cent. sodium chloride solution legumin is not precipitated by saturating the solution with magnesium sulphate, or sodium chloride. Saturated with sodium sulphate at 20°, no precipitate is produced; saturated at 25°, a turbidity appears; but saturated with sodium sulphate at 34°, all but a trace is thrown out of solution. By saturation with ammonium sulphate at common temperatures it is completely precipitated.

Dissolved in salt solution, legumin is not precipitated by mercuric chloride but gives a heavy precipitate on adding either picric, tannic, hydrochloric, nitric, sulphuric, or acetic acid.

In water containing a very small quantity of acid, legumin readily dissolves and is precipitated by adding sodium chloride. It is readily soluble in dilute alkalies and alkali carbonates.

Adding to its solution glacial acetic acid and concentrated sulphuric acid, a violet color is produced. With cupric sulphate and caustic potash, after standing, a crimson red color appears, almost as red as that given by peptones. With Mil-

lon's and the xantroprotein tests the usual reactions are given. When dissolved in ten per cent. sodium chloride solution and gradually heated, the solution becomes turbid at 97° and on long heating in a boiling water-bath, a coagulum gradually separates.

II. PROTEIDS OF THE VETCH.

One hundred grams of finely ground meal of the seed of the common vetch (*Vicia sativa*) were treated with water and the extract, after filtering clear, was saturated with ammonium sulphate. The small precipitate thereby produced was filtered out and dissolved in water; the resulting solution was filtered clear and dialyzed until free from chlorides. The globulin thus precipitated, after washing with water and with alcohol, weighed 1.04 grams. The meal residue was then treated repeatedly with ten per cent. sodium chloride solution and after filtering clear the extract was saturated with ammonium sulphate, the precipitated proteid filtered out and disssolved in brine. The resulting solution was filtered clear and dialyzed until free from chlorides. The globulin thus precipitated, when washed with water and alcohol, and dried over sulphuric acid, weighed five grams. When dried at 110° this preparation, 15, had the folling composition:

VETCH LEGUMIN, 15.

Carbon	52.45
Hydrogen	6.98
Nitrogen	18.04
Sulphur	0.50
Oxygen	22.03
	100.00
Ash	0.27

The meal residue was next treated with two-tenths per cent. potash water, the extract filtered clear and neutralized with very dilute hydrochloric acid; the precipitate thus produced was dissolved in two-tenths per cent. potash water, the clear solution was neutralized with dilute hydrochloric acid and the precipitated proteid washed with water and alcohol and dried. This preparation, 16, weighed four and four-tenths grams and gave the following results on analysis:

VETCH PROTEID, 16.

	I.	II.	Average.
Carbon	52.43	52.43	52.42
Hydrogen	7.13	7.02	7.07
Nitrogen	16.55	....	16.55
Sulphur } Oxygen }	....	....	23.96
			100.00
Ash			0.74

Four kilograms of vetch meal were next treated with twelve liters of ten per cent. sodium chloride brine and the residue washed with the same solution. The extract and washings were partly cleared by subsidence, then saturated with ammonium sulphate. The precipitate so produced was dissolved in brine, but the resulting solution was very difficult to filter. The greater part of the suspended impurities was removed by passing the extract through a loose bed of filter paper pulp and the proteid was again separated by saturation with ammonium sulphate. This precipitate was dissolved in brine and the solution, kept cold, then filtered perfectly clear. This solution was dialyzed in two portions, D and E. After nearly freeing from chlorides, a large precipitate formed in each dialyzer, which was filtered out. That obtained from E was washed with water and with alcohol as long as any coloring matter was extracted, and was then dried over sulphuric acid giving 120 grams of a slightly pink powder, which will be designated F. That from D was redissolved in ten per cent. sodium chlorine brine, the solution filtered perfectly clear and dialyzed until free from chlorides. All but a trace of proteid was thus thrown down. The precipitate was washed thoroughly with water and with alcohol and dried over sulphuric acid, yielding preparation 17, which weighed ninety grams and was very slightly colored. After drying at 110°, this preparation had the following composition:

VETCH LEGUMIN, 17.

	I.	II.	Average.
Carbon	51.98	51.97	51.98
Hydrogen	6.94	6.89	6.92
Nitrogen	17.96	18.00	17.98
Sulphur	0.45	....	0.45
Oxygen	....	....	22.67
			100.00
Ash			0.20

The filtrates from the first dialysis of solutions D and E were separately saturated with ammonium sulphate, the precipitates obtained were dissolved in water and the solutions filtered and dialyzed. The precipitate from D, thrown down by dialysis, was redissolved in salt solution and again precipitated by dialysis. The two preparations of globulin thus obtained were washed with water and with alcohol and dried over sulphuric acid, that from D weighed 4.11 grams, forming preparation 18, and that from E gave preparation 19, weighing 7.67 grams. On analyzing these preparations, dried at 110°, the following results were obtained:

VETCH LEGUMIN.

	18.	19.
Carbon	52.21	52.18
Hydrogen	6.82	6.82
Nitrogen	17.99	17.99
Sulphur	0.37	0.36
Oxygen	22.61	22.65
	100.00	100.00
Ash	0.23	0.12

The filtrate from the first precipitation by dialysis of 18 was united with the filtrate from 19 and the heat coagulation point determined in a portion of the solution, in which ten per cent. of sodium chloride had been dissolved. This solution became turbid at 56° and flocks separated at 63° in considerable quantity. After heating to 70° for some time and filtering, turbidity occurred on heating to 71° and a flocculent coagulum formed at 73°, about the same in amount as at 63°. After heating to 78° the solution was filtered and again heated, the turbidity forming a third time at 79° and flocks at 83° in smaller quantity than before. This slow and incomplete coagulation does not necessarily indicate the presence of several coagulable proteids in the solution, for there is no temperature interval between the successive coagula, the temperature at which turbidity occurs and a flocculent coagulum develops being determined, after the first coagulum has formed, by the temperature at which the solution was filtered. Each time the solution becomes turbid at a temperature just above that to which it had been previously heated and a flocculent coagulum separates at three or four degrees higher.

The presence of salts has much influence on the coagulation point, for another portion of this same solution, to which no salt had been added, became turbid at ten degrees lower than the portion wherein ten per cent. of sodium chloride had been dissolved and gave the last flocculent coagulum at a temperature ten degrees higher.

The solution, portions of which had served for the foregoing observations, was then dialyzed into alcohol until concentrated to one-half its original volume, when a considerable precipitate formed, which was filtered out, washed with alcohol, and dried over sulphuric acid. This substance consisted of a mixture of all the proteids remaining in solution after separating the globulin, as described. Any albumin or globulin which might be contained in this precipitate would probably be largely if not wholly coagulated by the long treatment with alcohol and the subsequent drying. This preparation was therefore very finely pulverized and extracted thoroughly with water. The insoluble residue was then washed with alcohol and dried, yielding 13.52 grams of preparation 20, which was found to have the following composition :

VETCH PROTEID 20.

	I.	II.	Average.
Carbon	53.45	53.65	53.55
Hydrogen	6.67	6.73	6.70
Nitrogen	16.46	....	16.46
Sulphur	1.02	....	1.02
Oxygen	....	....	22.27
			100.00
Ash	0.29		

The solution filtered from 20 was further dialyzed into alcohol and a second precipitate obtained, which, when washed with alcohol and dried, weighed 5.64 grams, and was composed as follows :

VETCH PROTEID, 21.

	I.	II.	Average.
Carbon	52.55	52.66	52.60
Hydrogen	6.70	6.95	6.83
Nitrogen	16.53	16.76	16.69
Sulphur	1.23	....	1.23
Oxygen	....	....	22.65
			100.00
Ash	0.65		

The filtrate from the precipitate produced by the first dialysis into alcohol, from which preparations 20 and 21 had been obtained, was further dialyzed into alcohol yielding a second precipitate which, when washed with alcohol and dried over sulphuric acid, weighed 2.21 grams and formed preparation 22. This consisted of proteose and, after drying at 110°, had the composition as follows:

VETCH PROTEOSE, 22.

	I.	II.	Average.
Carbon	50.95	50.76	50.85
Hydrogen	6.78	6.72	6.75
Nitrogen	16.53	16.79	16.65
Sulphur } Oxygen }	....	....	25.75
			100.00
Ash	2.18		

Comparing the composition of 21 with that of 20, it is seen that, excepting carbon, the figures agree quite well. 21, however, contains one per cent. less carbon than 20, which is easily explained by its being a mixture of the proteose represented by 22, and the proteid represented by 20. Such a mixture would be expected from the method of preparation.

If 20 is compared with 5 and 8, obtained in a similar manner from the pea, by dialysis of its extracts into alcohol, after precipitation of the greater part of the globulin contained in these extracts by dialysis in running water, it will be observed that they agree rather closely. It is hardly possible by this method to obtain entirely pure preparations, but our results show that the vetch and pea both contain another proteid that is different from legumin in composition and in properties.

To facilitate comparison these analyses are here tabulated.

	Pea proteid.		Vetch proteid.
	5.	8.	20.
Carbon	53.33	53.54	53.55
Hydrogen	6.93	6.99	6.70
Nitrogen	16.14	16.69	16.46
Sulphur	1.00	1.01	1.02
Oxygen	22.55	21.77	22.27
	100.00	100.00	100.00

It will be noted that this proteid contains more carbon and less nitrogen than legumin and nearly twice as much sulphur.

Whether it is a globulin soluble in extremely dilute salt solution or an albumin soluble in pure water, we have not as yet undertaken to ascertain, for want of time.

The residue of the meal extracted, as described, with salt solution, was treated with two-tenths per cent. potash solution, a portion of the alkali extract was filtered clear and neutralized with very dilute hydrochloric acid. The precipitate which resulted was dissolved in two-tenths per cent. potash water, and after filtering perfectly clear, again thrown down by neutralizing with hydrochloric acid. After drying 12.4 grams of 23 were obtained, having the following composition :

VETCH PROTEID, 23.

	I.	II.	Average.
Carbon	53.00	52.99	53.00
Hydrogen	6.91	7.02	6.97
Nitrogen	16.45	....	16.45
Sulphur	0.53	....	0.53
Oxygen	....	....	23.05
			100.00
Ash	0.92		

If this analysis is compared with that of 16, it will be noted that, although they agree in nitrogen content, they differ as respects carbon. The sulphur found in 23 would indicate that 23 is a mixture of legumin with other substances. It seems to us probable that it is mainly legumin which escaped extraction by the salt solution through imperfect pulverization of the meal or its incomplete exhaustion by the brine, or because it was present in the salt-insoluble form, a form which it may have assumed in the seed itself, or under the action of the solvents to which the meal was subjected. It has been our experience with other seeds that extractions with alkali, after exhausting the seed with salt solution, yields products which, in most cases, it is impossible to purify.

In order next to determine whether the legumin found in the vetch seed is a single proteid or a mixture, the following fractional precipitations were made.

One kilogram of the meal was extracted with ten per cent.

sodium chloride solution and, after filtering clear, the extract was saturated with ammonium sulphate and the proteids, thus precipitated, dissolved in 300 cc. of ten per cent. brine. The solution now measured 400 cc. and contained about eight per cent. of salt. After filtering perfectly clear, from a small amount of insoluble matter, an equal volume of distilled water was added. On standing a short time the proteid thus precipitated collected on the sides and bottom of the beaker as a sticky deposit, leaving the solution nearly clear. The latter was then decanted and the translucent, gummy mass of proteid washed with water, which caused it to turn opaque and become brittle, so that it was easily rubbed to a coarse powder.

After washing repeatedly with water the proteid was thoroughly washed with dilute alcohol, then with absolute alcohol, and dried over sulphuric acid. The preparation, 24, weighed 13.4 grams.

The solution decanted from 24 was cooled in an ice box over night and the clear supernatant liquid poured from the perfectly transparent semifluid layer which had thus formed on the bottom of the beaker. After washing and drying, 12.9 grams of preparation 25 were obtained. The solution decanted from 25 was mixed with an equal volume of distilled water and left over night in the ice box. A transparent layer of proteid was again deposited, which, when washed and dried, yielded 4.00 grams of 26.

The solution decanted from 26 was saturated with ammonium sulphate, the precipitated proteid dissolved in salt solution, and after filtering, the proteid was precipitated by dialysis. The globulin thus separated, after washing and drying, weighed 3.35 grams, and formed preparation 27.

The following figures were obtained by analyzing these preparations when dried at 110°.

VETCH LEGUMIN.

	24.	25.	26.	27.
Carbon	52.05	51.78	52.17	52.04
Hydrogen	6.99	6.89	6.92	7.06
Nitrogen	18.02	18.06	17.70	18.02
Sulphur	0.56	0.48	23.21	22.88
Oxygen	22.38	22.79		
	100.00	100.00	100.00	100.00

Several grams of preparation E, described on page 598, were dissolved in a little two-tenths per cent. potash water, the solution was diluted considerably with distilled water and carbon dioxide passed through it. At first the solution remained clear, but after a time the proteid suddenly and almost completely separated as a voluminous precipitate, the filtrate from which yielded but a trace of proteid on saturating with ammonium sulphate. The precipitate was washed with water and then treated with salt solution. A part dissolved and the rest was converted into a swollen gelatinous mass which rendered filtration impossible. After standing over night the solution was poured off and the gummy residue was washed by decantation, at first with salt solution and then with water. On washing out the salt, the residue lost its gummy character and became a dense, rapidly settling precipitate which was readily collected on a filter and completely washed with water and then with alcohol. After drying over sulphuric acid it furnished 2.62 grams of preparation 28. This peculiar behavior of legumin which has lost its solubility in salt solution, we have observed in a number of cases.

E, when treated directly with salt solution, behaved in exactly the same manner as the precipitate obtained by passing carbon dioxide through its solution in dilute potash water, that is, a part dissolved and a part remained as a gummy residue, which was dehydrated (?) by washing with water. The saline solution described above, which had been decanted from the part of the carbon dioxide precipitate which was insoluble in salt solution, was filtered clear and dialyzed free from chlorides. The precipitate which resulted was filtered out, washed and dried in the usual manner, and yielded 29. These two preparations were found to have the following composition :

VETCH LEGUMIN.

	28.	29.
Carbon	52.11	51.89
Hydrogen	6.82	6.88
Nitrogen	18.17	18.09
Sulphur	0.53	0.40
Oxygen	22.37	22.74
	100.00	100.00
Ash	0.27	0.13

Several grams of preparation 17 was dissolved in a little two-tenths per cent. potash water and the resulting clear solution was neutralized with dilute acetic acid, thereby precipitating the proteid. A portion of this precipitate was tested with ten per cent. sodium chloride solution and found to dissolve to a large extent and on warming to 50° nearly all went into solution. The remainder of the precipitate was washed, dried and analyzed with the following results:

VETCH LEGUMIN, 30.

Carbon	52.06
Hydrogen	6.80
Nitrogen	17.98
Sulphur	0.53
Oxygen	22.63
	100.00
Ash	0.15

Another portion of preparation 17 was dissolved in a little two-tenths per cent. hydrochloric acid and yielded a clear solution, which was neutralized with one-half per cent. sodium carbonate solution. The resulting precipitate was partly soluble in ten per cent. salt solution. It was washed and dried and, as preparation 31, gave the following figures when analyzed:

VETCH LEGUMIN, 31.

Carbon	52.12
Hydrogen	6.68
Nitrogen	18.20
Sulphur	0.40
Oxygen	22.60
	100.00
Ash	0.15

For convenience of comparison the analyses of legumin from the vetch are brought together in the following tables:

SUMMARY OF ANALYSES OF VETCH LEGUMIN.

	15.	16.	18.	19.	24.	25.
Carbon	52.45	51.98	52.21	52.18	52.05	51.78
Hydrogen	6.98	6.92	6.82	6.82	6.99	6.89
Nitrogen	18.04	17.98	17.99	17.99	18.02	18.06
Sulphur	0.50	0.45	0.37	0.36	0.56	0.48
Oxygen	22.03	22.67	22.61	22.65	22.38	22.79
	100 00	100.00	100.00	100.00	100.00	100.00

<table>
<tr><th></th><th>26.</th><th>27.</th><th>28.</th><th>29.</th><th>30.</th><th>31.</th></tr>
<tr><td>Carbon</td><td>52.17</td><td>52.04</td><td>52.11</td><td>51.89</td><td>52.06</td><td>52.12</td></tr>
<tr><td>Hydrogen</td><td>6.92</td><td>7.06</td><td>6.82</td><td>6.88</td><td>6.80</td><td>6.68</td></tr>
<tr><td>Nitrogen</td><td>17.70</td><td>18.02</td><td>18.17</td><td>18.09</td><td>17.98</td><td>18.20</td></tr>
<tr><td>Sulphur</td><td rowspan="2">23.21</td><td rowspan="2">22.88</td><td>0.53</td><td>0.40</td><td>0.53</td><td>0.40</td></tr>
<tr><td>Oxygen</td><td>22.37</td><td>22.74</td><td>22.63</td><td>22.60</td></tr>
<tr><td></td><td>100.00</td><td>100.00</td><td>100.00</td><td>100.00</td><td>100.00</td><td>100.00</td></tr>
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It will be seen from the following statement that the composition of legumin from the pea is identical with that from the vetch.

LEGUMIN.

	Pea. Average of 18 analyses on 10 preparations.	Vetch. Average of 13 analyses on 12 preparations.
Carbon	52.20	52.09
Hydrogen	7.03	6.88
Nitrogen	17.93	18.02
Sulphur	0.39	0.46
Oxygen	22.45	22.55
	100.00	100.00

What we have already stated concerning the properties and reactions of pea legumin applies strictly to that from the vetch except in two particulars. The solutions of pea legumin in ten per cent. brine when heated nearly to boiling become turbid and, after a time, a considerable coagulum separates in the form of a semi-solid clot. Similar solutions of the vetch legumin, on the other hand, remain perfectly clear, even after prolonged boiling.

Many carefully conducted experiments made with the legumin from each of these seeds, wherein the same quantity of globulin was dissolved in the same amount of salt solution of the same strength, were carried out side by side, but always with the same results, the pea legumin coagulating to a greater or less extent while the vetch legumin remained wholly unaffected.

That this difference is due to some foreign substance is indicated by the following experiment: A quantity of ten per cent. sodium chloride extract of pea meal was filtered clear and divided into two parts, one of which was dialyzed directly, the

other was saturated with sodium chloride and filtered clear. The latter solution was less viscid and much more easily filtered, presumably due to the removal of gum. This solution, saturated with salt, was then dialyzed.

The globulin precipitated by dialysis from each of the above named solutions, was dissolved in brine to new solutions containing ten per cent. of globulin and eight per cent. of sodium chloride. When these two solutions were heated, side by side, in the same water-bath and for the some length of time, a most marked difference was observed in the quantities of coagulum that appeared. Each solution contained a small quantity of the proteid coagulating at about 80°, so that after being heated to 85° for some time, they were filtered clear and again heated.

Each solution then became turbid at 93° and, after heating the bath to boiling for a little time, the solution of the globulin from the salt saturated extract became curdy, from the separation of a moderate quantity of coagulum, while that from the unsaturated extract set to a firm opaque jelly, so that the tube could be inverted without displacement of its contents.

The second difference noted was very slight, but appeared to be constant. By precipitating the legumin from the pea by dialysis, the proteid was obtained in the form of spheroids which showed little tendency to adhere in masses, while that from the vetch was always obtained in more or less coherent lumps which, however, were not at all fluid and gummy, but were easily broken up on stirring. In our opinion, the legumin from these two seeds is one and the same substance, or must, at least for the present, be so regarded.

SUMMARY.

1. So far as we have investigated, peas and vetches contain the same proteids, which are nearly if not entirely soluble in ten per cent. sodium chloride solution.

2. The greater part of these proteids consists of a globulin, the *Legumin* of Braconnot, which is readily precipitated by dialyzing its salt solutions.

The prevalent idea that legumin is soluble only in acids and alkalies is erroneous, it having been proved, notably by Ritt-

hausen, to be a true globulin. The composition of legumin, as shown by the average of our accordant analyses of thirty-one preparations obtained from the seeds of peas and vetches, is the following :

LEGUMIN.

Carbon	52.15
Hydrogen	6.96
Nitrogen	17.98
Sulphur	0.43
Oxygen	22.48
	100.00

Legumin is abundantly soluble in solutions containing above five per cent. of sodium chloride; in those containing less salt it is not so soluble, the amount held in solution decreasing as the salt content diminishes, so that it is but sparingly soluble in solutions containing less than one per cent. of salt. By dilution with water, strong saline solutions of legumin are abundantly precipitated.

By saturation with sodium chloride or magnesium sulphate, its sodium chloride solutions are not precipitated; by saturation with sodium sulphate at 25° they are not precipitated, but at higher temperatures more or less is thrown down, and by saturation with sodium sulphate at 34°, precipitation is very nearly complete. With nitric acid, Millon's and Adamkiewic's reagents it gives the usual proteid reactions.

With strong solutions of legumin the biuret test gives a violet color at first, which on standing becomes crimson red, similar to the color produced by peptones.

The legumin obtained by us from the vetch is not coagulated by heat nor even rendered turbid by prolonged boiling of strong solutions.

The legumin prepared by us from the pea is partly coagulated by heating strong solutions in a boiling water-bath, and sets to a firm jelly after thus heating for some time. These differences in their behavior on heating, and a greater tendency of the vetch legumin to cohere in semi-solid lumps when precipitated by dialysis, are the only points, of dissimilarity which a rigid comparison of preparations from the two seeds has revealed.

These differences, in our opinion, are due to the substances with which the proteid is associated in the two seeds, for saturation of the pea extracts with sodium chloride, before precipitating the legumin by dialysis, greatly diminished the amount of coagulum given by the pea legumin.

3. Besides the legumin, the pea and vetch contain another proteid in small amount, either an albumin or a globulin, soluble in extremely dilute salt solutions, and coagulated by heating its solutions to 80°. This substance we have not studied further than to make two preparations for analysis from the pea and one from the vetch. These were obtained in an insoluble form by coagulating with alcohol, so that the properties and reactions were not determined. The composition of this proteid is shown by the following average of three closely agreeing analyses:

PROTEID OF PEA AND VETCH.

Carbon	53.48
Hydrogen	6.89
Nitrogen	16.43
Sulphur	1.01
Oxygen	22.19
	100.00

4. In addition to the foregoing proteids a very little *proteose* was found in the extracts of both these seeds.

5. No attempt has yet been made to determine the total quantity of proteids in these seeds, nor to study minutely the proteids that occur in them in small proportion.

CONGLUTIN AND VITELLIN.[1]

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 21, 1896.

REVIEW of the literature relating to the plant proteids hitherto described as conglutin and vitellin, shows that the subject is in great confusion, which can only be cleared up by a thorough examination of the seeds from which these proteids are said to have been obtained. This is the more important, because of late years various investigations have been made in

[1] From the Report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

which these proteids have figured as the subject of study, while the fact, that the purity or even the identity of the proteid employed is very doubtful, has been entirely overlooked or ignored. Thus the results of observations on the globulin of lupins have been applied to the globulin of the squash, hemp and other seeds, it being apparently unknown that these two proteids are very distinct substances. Further, the composition and reactions of most of these bodies have never been adequately studied, nor the means of preparing them in a state of purity ascertained. Recent authors are mostly content to call these proteids vegetable vitellin and to assume, with little reason, that the proteid from the many seeds in which vitellin has been said to occur is one and the same substance. With the object of determining, so far as may be practicable, the true relations of the globulins found in the various seeds hitherto alleged to contain conglutin and vitellin, this investigation was undertaken.

ALMOMDS.

The proteid first discovered, which has since been known as conglutin, was found in the seed of the almond by Proust,[1] and by him named amandin.

Dumas and Cahours[2] described and analyzed preparations obtained from almonds, peach and plum seeds, and considered them to be legumin, identical with that of a large number of other seeds.

According to Rochleder[3] the proteid described by Dumas and Cahours is different from legumin as understood by Liebig and others. Norton[4] analyzed proteid preparations which he obtained from the almond and considered them to be legumin. Ritthausen[5] described the proteid of the almond under the name conglutin. He later[6] obtained from the peach kernel a proteid which he considered to be conglutin, identical with that of almonds and lupins.

The details of our investigation are as follows: A quantity of

[1] *J. de phys., de chim., d'histoire naturelle et des arts*, 54, 199.
[2] *J. prakt. Chem*, 28, 398.
[3] *Ann. der Chem. u. Pharm.*, 46, 155.
[4] *Am. J. Sci.*, [2], 5, 22.
[5] Eiweisskörper, Bonn, 1872.
[6] *J. prakt. Chem.*, 26, 422, *1882*.

sweet almond meats deprived of the brown skin (tegmen) were crushed and treated with ether to remove oil. Seventy-five grams of the oil-free meal was then extracted with ten per cent. sodium chloride solution, the extract was filtered clear and dialyzed until free from chlorides. The globulin separated at first in minute spheroids, which, on settling to the bottom of the dialyzer, united, forming a viscid semi-fluid translucent mass of a pale straw color. After decanting the solution, the globulin, which had separated, was again dissolved in ten per cent. sodium chloride brine and reprecipitated by dialysis. The proteid, obtained in the same condition as before, was washed with water, and with alcohol, dilute at first and afterwards gradually increased in strength, and finally was dehydrated with absolute alcohol and dried over sulphuric acid. This preparation, I, weighed 6.72 grams, was a snow white, dense powder, and, after drying at 110°, gave the following results on analysis:

AMANDIN, I.

				Average.
Carbon	51.49	51.32	....	51.41
Hydrogen	7.33[1]	6.86	....	6.86
Nitrogen	19.29	19.52	19.62	19.47
Sulphur	0.39	....	....	0.39
Oxygen	....	....	....	21.87
				100.00
Ash	0.24			

Another preparation of this globulin was made by crushing a quantity of fresh, shelled, "Jordan almonds," and extracting the oil with petroleum naphtha. After freeing from naphtha, the greater part of the skins was separated by sifting. 100 grams of the meal was then extracted with one liter of water and the solution filtered and saturated with ammonium sulphate. The precipitate produced was filtered out, dissolved in water, the resulting solution filtered perfectly clear and dialyzed until free from chlorides. The proteid, which on dialysis deposited with the same appearance and characters as the first preparation, was washed with water, dilute alcohol, stronger alcohol and then dehydrated with absolute alcohol and dried over sulphuric acid.

1 Omitted in average.

Sixteen grams were obtained, equal to sixteen per cent. of the meal. This preparation, owing to the seed-integument, which had been but partly removed, was somewhat red in color. After drying at 110°, analysis gave the following results:

AMANDIN, 2.

			Average.
Carbon	51.49	....	51.49
Hydrogen	6.85	....	6.85
Nitrogen	19.27	19.05	19.16
Sulphur	0.44	....	0.44
Oxygen	....	....	22.06
			100.00
Ash	0.80		

For a third preparation Jordan almonds were drenched with hot water for a moment to loosen the skins, which were then easily detached; the meats were squeezed in a drug press to separate the greater part of the oil. The remainder of the oil, after dehydrating the pressed meats with absolute alcohol, was extracted with naphtha. The residue was freed from naphtha by evaporation and ground to a fine powder. There was thus obtained from 900 grams of almonds 380 grams of oil-free meal. This was thoroughly extracted with ten per cent. sodium chloride brine and the extract filtered. A turbid liquid resulted which was saturated with ammonium sulphate. The proteid thus precipitated was dissolved in ten per cent. sodium chloride brine and the solution after filtering perfectly clear was dialyzed until nearly free from chlorides. The solution was then decanted from the semi-fluid, viscid precipitate which had formed, and this was washed with water and alcohol, dehydrated with absolute alcohol and dried over sulphuric acid. The proteid thus obtained weighed sixty-six grams. The filtrate from this preparation was saturated with ammonium sulphate, the precipitate was filtered out, dissolved in a little water and the filtered solution was dialyzed. This second dialysis yielded twenty-seven grams more of globulin which were added to that before obtained, making in all ninety-three grams, being twenty-four and one-half per cent. of the oil-free meal. Analysis of this preparation, 3, dried at 110°, gave results as follows:

AMANDIN, 3.

			Average.
Carbon	51.18	....	51.18
Hydrogen	6.99	....	6.99
Nitrogen	19.30	19.37	19.33
Sulphur	0.48	....	0.48
Oxygen	....	....	22.02
			100.00
Ash	0.35		

A portion of 3 was dissolved in sodium chloride solution and dialyzed into dilute alcohol in the hope of obtaining the globulin in the form of crystals. No distinct crystals resulted, and after remaining about two weeks in alcohol the precipitated proteid was readily redissolved in salt solution, not having been coagulated by the alcohol, and the clear solution was dialyzed in water until free from chlorides. After washing and drying in the usual manner this preparation, 4, was analyzed:

AMANDIN, 4.

	I.	II.	Average.
Carbon	51.39	51.32	51.36
Hydrogen	6.99	6.90	6.95
Nitrogen	19.32	19.36	19.34
Sulphur	0.45	....	0.45
Oxygen	....	....	21.90
			100.00
Ash	0.20		

PEACH KERNEL.

Ritthausen states that peach seeds contain the same proteid as the almond, a fact in harmony with the close botanical relations of the two plants.

We obtained this proteid from peach pits in the following manner: The seeds were freed from the skin (tegmen) by cutting it away with a knife and were then ground with ether to a powder and freed from oil. Only a small quantity of seeds, yielding but twenty grams of oil-free meal, were at the time available. This was extracted with ten per cent. sodium chloride solution and the clear filtered extract dialyzed. The globulin separated in spheroids, which settled to a translucent viscid semi-fluid mass like that from the almonds. The solution, when freed from chlorides

by dialysis, was decanted from the precipitate and the latter was washed with water, alcohol and absolute alcohol and dried over sulphuric acid; 2.44 grams or 12.2 per cent. of the meal were so obtained. Analysis of this preparation gave the following results:

AMANDIN, FROM THE PEACH, 5.

			Average.
Carbon	51.06	51.02	51.04
Hydrogen	6.86	6.79	6.83
Nitrogen	19.20	19.35	19.28
Sulphur	0.48	....	0.48
Oxygen	....	....	22.37
			100.00
Ash	0.62		

Owning to the small quantity of 5, it was not possible to compare its reactions throughout with those of amandin from the almond, but, so far as could be observed, the two were identical in all respects, and there can be no doubt that they are the same substance.

In the following table the foregoing results may be compared with those obtained by earlier investigators, in their work upon the proteid of the almond, peach and plum:

AMANDIN.

	Dumas and Cahours. Almonds.	Plums.	Löwenburg. Almonds.		Norton. Almonds.	
Carbon	50.89	50.93	51.10	50.50	50.97	49.16
Hydrogen	6.71	6.73	7.20	6.56	6.64	6.51
Nitrogen	18.93	18.64	....	17.33	17.15	17.43
Sulphur	....	....	....	0.32	0.27	0.41
Phosphorus	....	....	....	1.05	0.57	2.21
Oxygen	23.47	23.70	....	24.24	24.40	24.27
	100.00	100.00		100.00	100.00	100.00

Ritthausen.

	Almonds	Peach.
Carbon	50.44	50.82
Hydrogen	6.85	6.94
Nitrogen	18.61	18.60
Sulphur	0.43	0.32
Oxygen	23.67	23.32
	100.00	100.00

AMANDIN.

	Osborne and Campbell, Almonds.				Peach.	
	1	2	3	4	5	Average.
Carbon	51.41	51.49	51.18	51.36	51.04	51.30
Hydrogen	6.86	6.85	6.99	6.95	6.83	6.90
Nitrogen	19.47	19.16	19.33	19.34	19.28	19.32
Sulphur	0.39	0.44	0.48	0.45	0.44	0.44
Oxygen	21.87	22.06	22.02	21.90	22.37	22.04
	100.00	100.00	100.00	100.00	100.00	100.00

Amandin, that has been dried over sulphuric acid, when mixed with cold water dissolves to a very slight extent and forms a gummy plastic mass. In water heated to about 98° amandin melts to a transparent mass and a considerable portion goes into solution, which in part separates out on cooling, and is redissolved on heating again. Boiling the solution causes but a slight turbidity.

The precipitate formed by cooling the hot water solution of amandin, dissolves completely on addition of a little nitric acid, but if more nitric acid be added, a precipitate falls which dissolves on warming and reappears on cooling in exactly the manner of a proteose.

In ten per cent. sodium chloride solution this proteid dissolves readily to a slightly opalescent liquid, no insoluble "albuminate" being formed by drying, as is the case with most vegetable globulins.

A solution containing ten per cent. of amandin dissolved in ten per cent. sodium chloride brine gives an abundant precipitate when poured into much distilled water, but if only a small amount of proteid is dissolved in the brine no precipitate is produced by dilution.

Salt solution of amandin is not precipitated by saturating with sodium chloride. By saturating with magnesium sulphate it is partly thrown down. Saturation with sodium sulphate or ammonium sulphate completely precipitates it.

Nitric acid added to the sodium chloride solution forms a precipitate soluble in an excess of acid which, on heating, gives the usual xanthoprotein reaction.

With mercuric chloride solution no precipitate is formed.

With picric acid and also with tannic acid heavy precipitates are produced.

Amandin is readily soluble in very dilute acetic acid. The acetic solution yields an abundant precipitate with potassium ferrocyanide that is difficulty soluble in an excess of this salt to a solution precipitable by diluting with water. In concentrated glycerol the dry proteid dissolves quite readily, the clear solution yielding a considerable precipitate on adding absolute alcohol.

Concentrated hydrochloric acid dissolves it, with development of a violet-blue color on standing. By heating in quite dilute sulphuric acid a solution is obtained which becomes turbid on cooling, the proteid being far less soluble in sulphuric than in hydrochloric or acetic acids. With the biuret test and also with glacial acetic acid and concentrated sulphuric acid together, solutions of this globulin give a fine violet color.

After solution in very dilute potash water and precipitation by neutralizing with acetic acid, amandin retains its original solubility in salt solutions.

A ten per cent. sodium chloride solution, containing five per cent. of amandin, becomes turbid when heated to 75°, and at 80° flocks form in small quantity which slowly increase on gradually raising the temperature, but only a small part of the proteid is coagulated even by boiling.

Having thus, as we believe, established this proteid as a chemical species quite distinct from all others hitherto investigated, it is proper to restore the designation *Amandin* given it by Proust, its discoverer, and to discard for it the names vitellin and conglutin, which are associated with many erroneous statements as to its occurrence, composition and characters.

WALNUT, (*Juglans regia*).

Ritthausen[1] prepared the proteid from this seed, but owing to the large amount of tannin present in the skins, he found much difficulty in obtaining satisfactory results.

As Ritthausen's preparations differed widely in composition,

[1] *J. prakt. Chem.*, 24, 257.

and as he has published nothing respecting the properties of this proteid, we have made several preparations with the following results.

A quantity of walnut meats was crushed, freed from oil by extracting with petroleum naphtha, and the greater part of the skins removed by sifting. One hundred grams of this meal was then extracted with ten per cent. sodium chloride brine and, after filtering, eight-tenths of the salt solution applied was recovered as a clear extract corresponding to about eighty grams of meal. This was saturated with ammonium sulphate and the resulting precipitate filtered out and treated with salt solution. Much that failed to dissolve was separated by filtration and the clear solution was dialyzed until free from chlorides. During dialysis the proteid was deposited in spheriods which did not, like amandin, unite to a confluent mass. The precipitated globulin was then filtered out, washed with water, alcohol and absolute alcohol and dried over sulphuric acid. Only 2.87 grams was obtained, equal to about 3.6 per cent. of the meal. This small yield was undoubtedly due to tannin, which rendered the greater part of the proteid insoluble in salt solution.

Dried at 110° this preparation, 6, had the following composition:

WALNUT GLOBULIN, CORYLIN, 6.

			Average.
Carbon	50.32	50.32	50.32
Hydrogen	6.63	6.74	6.69
Nitrogen	19.06	19.12	19.09
Sulphur	....	....	23.90
Oxygen	....	....	
			100.00
Ash	0.63		

The part of the ammonium sulphate precipitate which was not taken up by salt solution at 20° was treated with brine at 60°. In this it dissolved almost completely and did not precipitate on cooling. The clear filtered solution was dialyzed free from chlorides, and by the usual process, 2.82 grams or 3.5 per cent. of globulin was obtained, having the following composition:

WALNUT GLOBULIN, CORYLIN, 7.

Carbon	50.83	
Hydrogen	6.79	
Nitrogen	19.05	19.04
Sulphur	0.89	
Oxygen	22.44	
	100.00	
Ash	0.15	

In order to avoid the presence of tannin, another lot of walnut seeds were drenched for a moment with hot water, whereupon the skins were easily stripped off. The crushed meats were then treated with ether to extract the oil and, after removal of ether by exposure to the air, the coarse meal was finely ground and fifty grams was extracted with 1500 cc. of ten per cent. brine of common salt. The extract was filtered clear, saturated with ammonium sulphate, the resulting precipitate dissolved in salt solution at 40° and the extract dialyzed free from chlorides. The precipitated globulin was then filtered out and treated in the usual manner, giving preparation 8, weighing ten grams, equal to twenty per cent. of the meal, and having the following composition:

WALNUT GLOBULIN, CORYLIN, 8.

			Average.
Carbon	50.77	50.74	50.76
Hydrogen	6.94	6.83	6.89
Nitrogen	19.10	19.02	19.06
Sulphur	....	....	23.29
Oxygen	....	....	
			100.00
Ash	0.32		

HAZEL-NUT OR FILBERT, (*Corylus tubulosa*).

Ritthausen[1] has detailed the results of his examination of the proteid of this seed and concluded it to be identical with the conglutin which he obtained from almonds.

In order to satisfy ourselves respecting this substance a quantity of hazel-nut meats was freed from skins and oil as already described in case of walnuts, and finely pulverized. The meal

[1] *J. prakt. Chem.*, 24, 257.

was then extracted with ten per cent. sodium chloride brine and the filtered extract saturated with ammonium sulphate. The precipitated proteid was filtered out, dissolved in salt solution, and the liquid, after filtering clear, was dialyzed free from chlorides.

During dialysis the globulin separated in spheroids which, like those of walnut globulin, settled down, without adhering together to a plastic mass, after the manner of amandin. The precipitated globulin was filtered out and treated in the usual way. When dried at 110° this preparation had the following composition :

CORYLIN, FILBERT GLOBULIN, 9.

			Average.
Carbon	50.64	50.80	50.72
Hydrogen	lost	6.86	6.86
Nitrogen	19.14	19.19	19.17
Sulphur	0.83	....	0.83
Oxygen	....	....	22.42
			100.00
Ash	0.28		

In properties this preparation exactly resembled the globulin obtained from the walnut. That the two are identical in composition is shown by the following statement :

CORYLIN.

	Walnuts 6	Walnuts 7	Walnuts 8	Filberts. 9
Carbon	50.32	50.83	50.76	50.72
Hydrogen	6.69	6.79	6.89	6.86
Nitrogen	19.09	19.05	19.06	19.17
Sulphur } Oxygen }	23.90	0.89 } 22.44 }	23.29	0.83 22.42
	100.00	100.00	100.00	100.00

The properties of this proteid, after drying over sulphuric acid, as exhibited by preparations 8 and 9, are as follows. In the dry state it forms a heavy snow-white powder which, unlike amandin, is entirely insoluble in distilled water at 20° or at 40°. In ten per cent. sodium chloride solution it dissolves readily and completely, as also in exceedingly dilute acids and alkalies. Sulphuric acid, however, dissolves it much less readily than acetic, hydrochloric or nitric acid.

The solution in ten per cent. sodium chloride brine, containing ten per cent. of this globulin, gives an abundant precipitate when diluted with an equal volume of water. More dilute solutions give precipitates on sufficient dilution. Corylin is very much more readily precipitated by dilution than amandin. Hydrochloric acid and acetic acid each gives a precipitate insoluble in considerable excess of acid, when added to saline solutions of the proteid. With mercuric chloride, picric acid, or tannic acid dissolved in ten per cent. sodium chloride brine, heavy precipitates are produced. Saturation with sodium chloride gives a slight precipitate. Saturation with magnesium sulphate produces a considerable though partial precipitation. Saturation with sodium sulphate or ammonium sulphate effects a complete precipitation.

Dissolved in a little acetic acid, a precipitate is produced by sufficient nitric acid, which dissolves on heating and partly reprecipitates on cooling, The solution in acetic acid gives a precipitate with potassium ferrocyanide, but slightly soluble in a large excess of the latter.

With the biuret test the usual violet color is obtained. With Millon's and the xanthoprotein tests the ordinary proteid reactions appear. Dissolved in concentrated hydrochloric acid and boiled, a violet blue color develops on standing.

With glacial acetic acid and concentrated sulphuric acid, solutions of corylin give a violet color. When five per cent. of this proteid is dissolved in ten per cent. sodium chloride brine and the solution heated, turbidity ensues at about 80° and flocks form in small amount at 99°. On boiling the solution, a little more coagulates, but the corylin is precipitated by heat very slowly and incompletely.

When dissolved in dilute potash water and precipitated by neutralization, the proteid dissolves completely in ten per cent. salt solution. These reactions and the results of analysis show this body to be entirely distinct from either amandin or edestin. We therefore propose the name *Corylin*, from the generic name of the filbert, *Corylus tubulosa*, in which this proteid was first found by Dumas and Cahours.[1]

[1] *J. prakt. Chem.*, 28, 398.

BRAZIL-NUT, (*Bertholletia excelsa*).

Weyl[1] described the globulin of the Brazil-nut under the name of vegetable vitellin, and first determined its composition with a close approach to accuracy.

One of us has already investigated this substance as to its composition and properties, when prepared both in the form of spheroids and as perfectly distinct crystals.[2] This proteid, being evidently different from all others hitherto examined, deserves a distinct name, and we accordingly propose to designate it *Excelsin*.

OAT-KERNEL.

From the oat-kernel one of us[3] obtained a crystallized globulin very similar in composition to excelsin, but different in its reactions as well as in crystalline form. This globulin might be classed as a vitellin, and for that reason is here referred to. As yet this proteid has received no specific name and we now propose to call it *Avenalin*.

HEMP, (*Cannabis sativa*), SQUASH, (*Cucurbita maxima*), AND CASTOR BEAN, (*Ricinus communis*).

Proteid preparations from the seeds of hemp, squash and castor bean have been described under the names of conglutin and vitellin. One of us[4] has shown that these seeds contain, as their chief and characteristic proteid, one and the same substance and has named it *Edestin*. This has been found in a larger number of seeds than any proteid yet discovered, and is the body most commonly called vegetable vitellin. It is readily obtained pure in octahedral crystals, from several seeds, and owing to this fact has been employed in physiological investigations. That it is a different substance from the proteids already described in this article appears to have been mostly overlooked. The properties and composition of edestin are detailed in the paper above mentioned, and in the annual reports of Connecticut Experiment Station for 1893, pp. 179, 214, 216, and 1894, pp. 155, 170, 190.

COCOANUT, (*Cocos nucifera.*)

The proteid of the cocoanut was examined by Ritthausen[5]

1 *Ztschr. phys. Chem.* 1, 85.
2 Osborne: *Am. Chem. J.*, 14, 662.
3 Osborne: Reports of Connecticut Experiment Station 1890 and 1891, and *Am. Chem. J.*, 14, 212 and 682.
4 Osborne: *Am. Chem. J.*, 14, 671–689.
5 Pflüger's Archiv., 21, 96.

who, without identifying it with conglutin, assigned to it a similar composition. Chittenden[1] under the general name phytovitellin, gives the composition of this proteid in close accord with that of edestin, and as he obtained it partly crystallized in octahedra it probably is edestin.

LUPIN (*Lupinus.*)

The principal proteid contained in lupin seeds is the body to which Ritthausen first gave the name conglutin.[2] We have devoted much labor to the study of this proteid, but the results of our work are not yet complete and will form the subject of a future paper. We find that it is distinctly different in composition and properties from the proteids which we have hitherto noticed, and we take especial pleasure in confirming to it the name *conglutin* proposed by its veteran discoverer.

We give on the following page the composition of conglutin as found by us in accordant analyses of six preparations from the blue lupin.

SUNFLOWER (*Helianthus.*)

The proteid of the sunflower seed as described by Ritthausen[3] appears to be identical with edestin, but our investigation of this substance, which is still in progress, shows that the proteid prepared by the usual methods is contaminated with the helianthotannic acid described by Ludwig and Kromayer.[4] As yet we have been unable to obtain this proteid in the pure state.

To the best of our knowledge the proteids noticed in this paper include all which have been hitherto designated either as conglutin or vitellin. Of late years many seeds have been described as containing vitellin, but its presence has been inferred from qualitative reactions and not, except in those cases mentioned in this paper, from a study of the isolated proteid.

We have accordingly at least six perfectly distinct proteids which have been confounded together under the name vitellin or conglutin. The following table shows the present state of our knowledge concerning the composition of these globulins and sets forth the characters in whlch they have been found to differ.

1 Medical Record, 45, 450, and Digestive Proteolysis, New Haven, 1895, p. 32.
2 Eiweisskörper, Bonn, 1872, and *J. prakt. Chem.*, 25, 422.
3 Pflüger's Archiv., 21, 81.
4 N. Br. Arch., 99. 1 and 285.

PROTEIDS FORMERLY KNOWN AS VITELLIN OR CONGLUTIN.

	Edestin.	Amandin.	Corylin.	Excelsin.	Avenalin.	Conglutin.
Carbon.................	51.65	51.30	50.72	52.18	52.18	51.00
Hydrogen.............	6.89	6.90	6.86	6.92	7.05	6.90
Nitrogen..............	18.75	19.32	19.17	18.30	17.90	17.99
Sulphur...............	0.85	0.44	0.83	1.06	0.53	0.40
Oxygen...............	21.86	22.04	22.42	21.54	22.34	23.71
	100.00	100.00	100.00	100.00	100.00	100.00
Salt solution saturated with:						
Sodium chloride.	No pp.	No pp.	No pp.	No pp.	Complete pp.	No pp.
Magnesium sulphate.	Complete pp.	Partial pp.	Partial pp.	Slight pp.	Complete pp.	No pp.
Mercuric chloride.	Pp.	No pp.	Pp.	No pp.	Pp.	No pp.
Solution of ten per cent. proteid and ten per cent. sodium chloride diluted with equal volume of water gives:	Pp.	No pp.	Pp.	Slight pp.	Pp.	No pp.
Heat coagulation:					No coagulation even on boiling.	Trace of coagulation at 99°, sets to jelly on cooling.
Turbidity.	88°	75°	80°	70°		
Flocks.	95°	80°	99°	84°		
Precipitate by dialysis:	Octahedral crystals or spheroids, pulverulent.	Spheroids, uniting to viscid semi-fluid.	Spheroids, pulverulent.	Hexagonal plates or spheroids, pulverulent.	Spheroids, pulverulent.	Spheroids uniting to plastic mass.
Found in seeds of:	Hemp, Castor bean, Squash, Flax, Cotton, Wheat, Rye, Barley, Maize, Cocoanut.	Almond, Peach.	Walnut, Filbert	Brazil-nut.	Oat.	Lupin.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 21.]

THE CHEMISTRY OF THE CACTACEAE.[1]

BY ERVIN E. EWELL.

Received May 13, 1896.

I. AN HISTORICAL RESUMÉ AND PRELIMINARY NOTE.

THERE is probably no more interesting family of plants than the *Cactaceae*. This interest is manifest among civilized and uncivilized peoples, old and young, scientific and unscientific. If there is one that does not feel this interest; if there is one that is not inspired with awe at the mere contemplation of the weird forms assumed by the numerous species of this great order, which includes giants and the tiniest dwarfs; if there is one that is not moved by the mysterious beauty of an opening blossom of the "night-blooming cereus," then let that one swallow one or more of the little buttons that we shall exhibit to you this evening and note whether or not he is susceptible to the more subtle and more powerful influence that he will find working from within. There is scarcely a housewife in the land that pretends to maintain a conservatory or a window garden without numbering one or more cacti in her collection. She would have no hesitation about pronouncing any member of the order a cactus, so marked are their characteristics; yet, when it comes to a more minute study for purposes of classification, botanists who have spent years in studying them are still disputing about them and have filled the literature of the subject with a host of synonymous names.

When we examine the chemical side of the subject, we find that our knowledge is still more imperfect. The fact that many of these plants are used for food and that their juices are drunk in place of water by the travellers in the arid regions where they grow in abundance, has caused them to be regarded as devoid of chemical constituents of greater importance than those that are to be expected in any of the innocent plants of humid regions. Various species have been used medicinally in the countries in which they grow. *Cereus grandiflorus* and a few allied species have attained a reputation in medical practice

[1] An abstract of this paper was read before the Washington Section of the American Chemical Society, April 9, 1896.

among peoples more advanced in the scale of civilization, and have consequently been made the subject of some chemical investigation. Their fresh juices produce irritation of the skin when locally applied, and preparations of them are administered internally as cardiac stimulants and for other purposes. The first article published in this country on the subject seems to have been one by A. F. Pattee, which appeared in the *Boston Medical and Surgical Journal* in 1867. O. M. Meyers published an article in the *New York Medical Journal* in 1891, in which he called attention to the value as a heart tonic of a preparation of *Cereus grandiflorus* called "cactina." This was claimed to be the active principle of the drug, but it was not stated whether it was alkaloidal, glucosidal, or of some other nature. Numerous papers quickly followed, containing reports of clinical experiments with this and other preparations of the drug. Some of these papers included brief reports of chemical investigations. Boinet and Boy-Tessier reported the finding of an alkaloid in this species.[1] G. Sharp[2] stated that he was unable to find either alkaloid or glucoside in the drug, and ascribed any active properties that it may have to the resin that it contains. He failed to obtain any marked effect from the drug itself, and took doses of forty and one hundred of the cactus pills, prepared from *Cactus Mexicana*, without result. This is practically all that has been done in the way of chemical investigation of this class of plants in recent years, excepting the species that we are to consider and a few species closely related thereto.

As far as I have been able to learn, three groups of persons have been especially active in the scientific study of the *Cactaceae* during the last decade: First, a group of persons at Berlin, the center of which is Dr. L. Lewin, whose earlier work has been reported in this country in a pamphlet published by Parke, Davis & Co., of Detroit, and in the *Therapeutic Gazette* for 1888; second, a group of persons at the Pharmacological Institute of the University of Leipsic, where the work has been conducted by Dr. Arthur Heffter; third, a group of persons in this city, centering in the Bureau of American Ethnology, and including

1 *Bulletin général de Therapeutique, 1891*, 121, 343-349.
2 *London Practitioner*, 1894.

as associates the Division of Chemistry of the Department of Agriculture for chemical studies, Drs. Prentiss and Morgan for the study of physiological properties, and the Botanical Division of the Department of Agriculture for the settlement of botanical questions. These more recent investigations have been directed toward one or more species of cacti that are used by the American Indians for ceremonial and medicinal purposes. This substance, known as "mescal buttons" in the commerce of our southwestern border and in Mexico as *peyote* or *pellote*, has been of commercial and medicinal importance in Mexico for many years, being mentioned by Spanish writers as early as 1790. It was included in the Mexican Pharmacopoeia of 1842, but has been omitted from the later editions. The species furnishing the "mescal buttons" is *Anhalonium Lewinii* (Hennings), for which the synonymous names are *Anhalonium Williamsii*, var., *Lewinii* and *Lophophora Williamsii*, var., *Lewinii*. There seems to be evidence that *Anhalonium Williamsii* also contributes to the supply of "mescal buttons" and *pellote*. This latter species is likewise burdened with an abundance of names, being known among botanists by the names of *Echinocactus Williamsii* and *Lophophora Williamsii*, in addition to the one just used to designate it.

For a detailed account of the use of the dried "buttons" by the Indians, I quote, by permission, from a recent article on the subject by Mr. James Mooney of the Bureau of American Ethnology:[1]

"About five years ago, while making investigations among the Kiowa Indians on behalf of the Bureau of Ethnology, the attention of the writer was directed to the ceremonial use of a plant for which were claimed wonderful medical and psychologic properties. So numerous and important are its medical applications, and so exhilarating and glorious its effect, according to the statements of the natives, that it is regarded as the vegetable incarnation of a deity, and the ceremonial eating of the plant has become the great religious rite of all the tribes of the southern plains. * * * * * * * * *

[1] The Mescal Plant and Ceremony, by James Mooney. *Therapeutic Gazette*, January, 1896.

"As a matter of fact, there are several varieties, probably all of the same genus, used by the Indians in a ceremonial way. The explorer Lumholtz mentions three varieties among the Tarahumari of northern Mexico, (see his article in *Scribner's Magazine* for October, 1894). A different sort, from the lower Rio Grande, is used by the Kiowas and associated tribes, and a smaller variety is found among the Mescalero Apaches of eastern New Mexico. In each language it has a different name, usually referring to the prickles. Among the Kiowas it was *señi*; among the Comanches, *wokowi*; with the Mescaleros, *ho*; and with the Tarahumaris, *hikori*. The traders of the Indian Territory commonly call it mescal, although it must not be confounded with another mescal in Arizona, the *Agave*, from which the Apaches prepare an intoxicating drink. The local Mexican name upon the Rio Grande is *peyote* or *pellote*, from the old Aztec name *peyotl*.

"The use of the plant for medical and religious purposes is probably as ancient as the Indian occupancy of the region over which it grows. There is evidence that the ceremonial rite was known to all the tribes from the Arkansas to the valley of Mexico, and from the Sierra Madre to the coast. The Mescalero Apaches take their name from it. Personal inquiry among the Navajos and Mokis proved that they had no knowledge of it.

"In proportion as the plant was held sacred by the Indians, so it was regarded by the early missionaries as the direct invention of the devil, and the eating of the peyote was made a crime equal in enormity to the eating of human flesh. From the beginning it has been condemned without investigation, and even under the present system severe penalties have been threatened and inflicted against Indians using it or having it in their possession. Notwithstanding this, practically all the men of the Southern Plains tribes eat it habitually in the ceremony, and find no difficulty in procuring all they can pay for. In spite of its universal use and the constant assertion of the Indians that the plant is a valuable medicine and the ceremony a beautiful religious rite, no agency physician, post surgeon,

missionary, or teacher—with a single exception—has ever tested the plant or witnessed the ceremony.

"A detailed account of mythology, history and sacred ritual in connection with the mescal would fill a volume. Such an account, to be published eventually by the Bureau of Ethnology, the writer is now preparing, as the result of several years of field study among the Southern Plains tribes.

"The ceremony occupies from twelve to fourteen hours, beginning about nine or ten o'clock and lasting sometimes until nearly noon the next day. Saturday night is now the time usually selected, in deference to the white man's idea of Sunday as a sacred day and a day of rest. The worshippers sit in a circle around the inside of the sacred tipi, with a fire blazing in the center. The exercises open with a prayer by the leader, who then hands each man four mescals, which he takes and eats in quick succession, first plucking out the small tufts of down from the center. In eating, the dry mescal is first chewed in the mouth, then rolled into a large pellet between the hands, and swallowed, the man rubbing his breast and the back of his neck at the same time to aid the descent. After the first round the leader takes the rattle, while his assistants take the drum, and together they sing the first song four times, with full voices, at the same time beating the drum and shaking the rattle with all the strength of their arms. The drum and rattle are then handed to the next couple, and so the song goes on round and round the circle—with only a break for the baptismal ceremony at midnight, and another for the daylight ceremony—until perhaps nine o'clock the next morning. Then the instruments are passed out of the tipi, the sacred foods are eaten, and the ceremony is at an end. At midnight a vessel of water is passed around, and each takes a drink and sprinkles a few drops upon his head. Up to this hour no one has moved from his position, sitting cross-legged upon the ground and with no support for his back, but now any one is at liberty to go out and walk about for a while and return again. Few, howover, do this, as it is considered a sign of weakness. The sacred food at the close of the ceremony consists of parched corn in sweetened water; rice or other boiled grain; boiled fruit, usually now prunes or

dried apples; and dried meat pounded up with sugar. Every person takes a little of each, first taking a drink of water to clear his mouth.

"After midnight the leader passes the mescal around again, giving to each man as many as he may call for. On this second round I have frequently seen a man call for ten and eat them one after the other as rapidly as he could chew. They continue to eat at intervals until the close. There is much spitting, and probably but little of the juice is swallowed. Every one smokes hand-made cigarettes, the smoke being regarded as a sacred incense. At intervals some fervent devotee will break out into an earnest prayer, stretching his hands out toward the fire and the sacred mescal the while. For the rest of the time, when not singing the song and handling the drum or rattle with all his strength, he sits quietly with his blanket drawn about him and his eyes fixed upon the sacred mescal in the center, or perhaps with his eyes shut and apparently dozing. He must be instantly ready, however, when his turn comes at the song, or to make a prayer at the request of some one present, so that it is apparent that the senses are always on the alert and under control of the will.

"There is no preliminary preparation, such as by fasting or the sweat-bath, and supper is eaten as usual before going in. The dinner, which is given an hour or two after the ceremony, is always as elaborate a feast as the host can provide. The rest of the day is spent in gossiping, smoking, and singing the new songs, until it is time to return home. They go to bed at the usual time, and are generally up at the usual time the next morning. No salt is used in the food until the day after the ceremony.

"As a rule, only men take part in the regular ceremony, but sick women and children are brought in, and, after prayers for their recovery, are allowed to eat one or more mescals prepared for them by the priest."

It is to Mr. Mooney that we are indebted for the commencement of the scientific study of the drug in this country. On his return in the summer of 1894, from a prolonged residence among the tribes that use the drug, he brought with him a considerable

quantity of the dried "buttons" for use in scientific investigations. A portion of this material was turned over to Dr. H. W. Wiley, Chief of the Division of Chemistry of the Department of Agriculture, for a study of its chemical constituents. This task was assigned to the author by Dr. Wiley in September, 1894. The only literature of the subject at hand at that time was the article published by Dr. Lewin in 1888,[1] in which he announced the discovery and name, anhalonin, of an alkaloid in *Anhalonium Lewinii*, a name that had been given to the plant furnishing "mescal buttons" by Hennings, the botanist to whom Lewin intrusted the botanical identification of the crude material in which the alkaloid was found. Work had hardly been begun in the laboratory of the Department of Agriculture with the result of the separation of a considerable portion of Lewin's anhalonin, when Dr. Heffter[2] published an article in which he reported the results of a chemical study of four species of the genus Anhalonium: *A. fissuratum*, *A. prismaticum*, *A. Williamsii*, *A. Lewinii*. This was quickly followed by a report by Lewin of the continuation of his experiments mentioned above.[3]

For the aid of the American readers who may feel an interest in this subject, the writer has prepared the following table, in which the results of the investigations, hitherto reported, of the three more thoroughly studied species of anhalonium, are presented in a convenient form for reference and comparison:

1 *Archiv für experimentelle Pathologie und Pharmakologie, 1888*, 24, 401; *Therapeutic Gazette, 1888*, p. 232, and in a pamphlet issued by Parke, Davis & Co., of Detroit, the same being a reprint from "The Pharmacology of the Newer Materia Medica."

2 *Archiv für experimentelle Pathologie und Pharmakologie, 1894*, 34, 65–86.

3 *Archiv für experimentelle Pathologie and Pharmakologie*, 1894, 34, 374–391.

Species.	A. fissuratum.	A. Williamsi.	A. Lewinii.					
Investigators.	Heffter, 1894.	Heffter, 1894.	Heffter, 1894.			Lewin, 1888.	Lewin, 1894.	
Names of bases reported.	Anhalin.	Pellotin.	Alkaloid A.	Alkaloid B.	Alkaloid C.[1]	Anhalonin.	Crystalline anhalonin.[2]	Amorphous anhalonin.[2]
Formulas of bases analyzed.	$C_{10}H_{17}NO$.	$C_{13}H_{21}NO_3$.					$C_{12}H_{15}NO_3$.	
Crystalline form.	Crystals were obtained by adding NH_4OH to the concentrated water solution of the s'lp'te. White, opaque, adherent prisms, 2 mm. long, group'd in star forms.	Separates from alcohol in beautiful transparent tables that lie upon one another in cubical aggregates. It was crystallized from petroleum ether.	Sirupy, did not crystallize.	Sirupy, did not crystallize.	Sirupy, did not crystallize.	Sirupy, did not crystallize.	From aqueous solution, partly prismatic with irregularly pointed ends; partly tabular combinations; rhombic system. Crystals from ethereal solution gradually turn yellow.	Was not obtained in the crystalline state.
Solubility.	Cold water, very slight; more soluble in hot water; readily sol'ble in alcohol, methyl alcohol, ether, and petroleum ether.	Soluble in water by long boiling; soluble in alcohol, ether, acetone, chloroform, and petroleum ether.					Soluble in a large quantity of water; uncommonly easily soluble in alcohol, ether, chloroform, and benzene.	Same solubilities as the crystalline base.
Melting-point.	On platinum foil, melts to a clear, bright-yellow liquid, which gives off vapors having no characteristic odor; in a tube it melts quietly without decomposition at 115°, and crystallizes on cooling.	On platinum foil, melts to a bright-yellow liquid, with the formation of vapors having the odor of volatile amine bases; in a tube melts at 110°.					Softens at 74° and is liquid at 77.5°. It can be sublimed without decomposition.	

[1] Contained in the uncrystallizable mother-liquor remaining after the crystallization of the sulphates of alkaloid A and B.

[2] Prepared by E. Merck & Co.

Taste.	Aqueous solutions of the salts of this base have a bitter, saline taste, resembling that of potassium iodid.	Intensely and persistently bitter.						
Reactions with alkaloidal precipitants								
$KI + HgI_2$.	Amorphous precipitate.	Amorphous precipitate, becoming short, thick prisms.	Snow-white, well-formed microscopic tables.	Citron-yellow, crystalline precipitate, composed of short needles grouped in clusters.				
$KI + BiI_3$.	Amorphous precipitate.	Amorphous precipitate, becoming orange red, curved needles.	Amorphous precipitate.	Amorphous red-brown precipitate.				
$KI + CdI_2$.		Amorphous precipitate, becoming colorless, right-angled tables that lie upon each other in such a maner as to form peculiar dendritic figures.	No precipitate.	No precipitate.	A precipitate is formed.			
$KI + I_2$.	Brown drops separate, which solidify to prisms after a time.	Amorphous precipitate, becoming bright-brown, long, thin needles.	Very thin, long needles of a beautiful steel-blue color.	Amorphrus, fire-red precipitate.		Amorphous, brown-red precipitate.	Very small brown needles	
Phosphotungstic acid.	Amorphous precipitate.	Amorphous precipitate.	Amorphous precipitate.	Amorphous, yellow-white precipitate.		Crystalline, white precipitate.	Amorphous, white precipitate.	Amorphous, white precipitate.

Phosphomolybdic acid.	Amorphous precipitate.	Amorphous precipitate.	Amorphous precipitate.				Amorphous, yellow precipitate.	Amorphous, yellow precipitate.
$PtCl_4$.	No precipitate in aqueous solution; a precipitate separates in the form of drops from the alcoholic solution.	From weak alcoholic solution, forms golden yellow, fern-like aggregates of crystals.	Bright-yellow, fine needles,, grouped in the form of sheaves. This precipitate is very insoluble in water.	Short, broad, obliquely cut prisms.		Flaky crystals after shaking.	Bright-yellow precipitate, which arranges itself in clusters of crystals.	Amorphous, yellow-brown precipitate.
$AuCl_3$.	The same as with $PtCl_4$.	No precipitate. (?)	No precipitate.	No precipitate.	Precipitate.	Crystalline, brown-red precipitate.	Yellow-brown, beautifully-formed crystals.	Amorphous, brown precipitate.
$HgCl_2$.	The same as with $PtCl_4$.							Amorphons, white precipitate.
Picric acid.		Amorphous precipitate, becoming star-formed groups of prismatic needles.	No precipitate.	No precipitate.	Precipitate.	Yellow, crystalline precipitate.	Bright-yellow, amorphous precipitate that becomes crystalline on standing.	Bright-yellow, amorphous precipitate.
Tannic acid.		No precipitate.	No precipitate.	No precipitate.		Yellowish-white, amorphous precipitate.	White, amorphous precipitate.	
$AgNO_3$.							White, amorphous precipitate in solutions of the free base.	
$K_2Cr_2O_7$.							In concentrated solution dendritic crystals are formed after some time.	Amorphous, brown-red precipitate.

$FeCl_3$.							Immediately after the addition of the reagent there is formed a thick mass of yellow-white, long prismatic crystals.	No precipitate.
NH_4CNS.							No precipitate.	Amorphous, brown precipitate.
Color reactions.								Similar to anhalonin.
H_2SO_4.	Quickly dissolves with no color in the cold or on heating.	Dissolves with a slight yellow color that is not altered by standing or warming.					Is colored yellow and on heating turns to a violet-red color that is very persistent.	
HCl.	The same as with H_2SO_4.							
H_2SO_4 + HNO_3.	A drop of HNO_3 added to the H_2SO_4 solution produces a green color.	The crystal dissolves with a brown-red color that changes to an intense permanganate color on warming.	The same as with pellotin.	The same as with pellotin.		A permanganate color which turns yellow after some time.	A deep violet-red which soon becomes br'wn and finally colorless.	
HNO_3.		The same as with H_2SO_4 + HNO_3.	The same as with H_2SO_4 + HNO_3.				A light-red, then blood-red, which turns yellow on warming.	

HNO_3 followed by KOH	A small crystal warmed on the water-bath with one to two drops of HNO_3 forms a yellow solution, that is turned a persistent orange-red by an excess of solution of KOH.							
Cl_2.							Chlorin water turns an aqueous solution light yellow; on warming this becomes rose-red and changes to green on long standing.	
SALTS.					No crystallizable salt was obtained.			
Hydrochlorate.	$C_{10}H_{17}NOHCl$.							
Crystalline form.	On adding ether to the solution of the salt in absolute alcohol, small, shining, tabular crystals were obtained.	Hard prisms					This salt crystallizes from the aqueous solution more readily than the free base. It forms colorless, six-sid'd prisms of the rhombic system, 0.3-0.7 mm. broad and 5-7 mm. long. Their terminations are sometimes pointed and sometimes basal planes.	A brown, very hygroscopic amorphous powder.

Solubility.	Very readily soluble in water, alcohol, and methyl alcohol.	Very easily soluble in water.					Slightly soluble in cold water; easily soluble in hot water, forming a neutral solution: soluble in alcohol.	
Melting-point							Melts at 254-255° with decomposition.	
Specific rotatory power.							$[\alpha]^{25}_{D}=-40.56$ Concentration was 1.333 g'm's in 100 cc. of 50 per cent. alcohol.	
Taste.							Slightly bitter.	Very bitter.
Sulphate.	$(C_{19}H_{17}NO)_2.H_2SO_4+2H_2O$.							
Crystalline form.	Colorless, shining, very thin tables were obtained by crystallization from alcohol.	Not obtained in crystalline form.	Colorless, shining needles.	Small, white, non-lustrous, rhombic tables.				
Solubility.	Very easily soluble in cold water: less readily sol'ble in cold alcohol but readily soluble in hot, ninety per cent alcohol.		Difficultly soluble in cold water, easily soluble in hot water; almost insoluble in alcohol.	More readily soluble in cold water than alkaloid "A."				

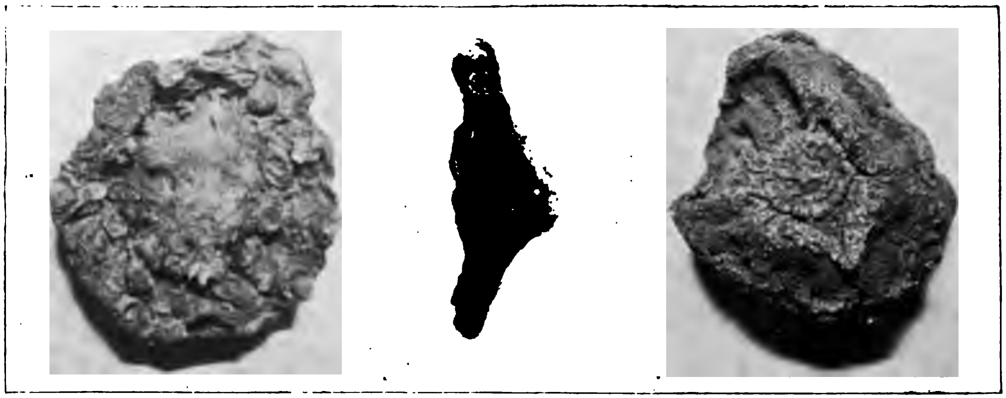
Melting-point	Melts without coloration at 197°.		169°.	220°.				
Oxalate.	$(C_{10}H_{17}NO)_2(COOH)_2$.							
Crystalline form.	Readily crystallized from hot alcohol in a form similar to that of the sulphate.	Needles.						
Solubility.	Similar to anhalin sulphate.	Very easily soluble in cold water; insoluble in alcohol.						

All of the bases mentioned in the above table are possessed of marked physiological properties, and produce death when administered to the lower animals in sufficient doses. The nature and extent of the physiological activity of these alkaloids as determined by the experiments of Lewin and Heffter, are shown in the following table :

II. Table Showing the Nature and Intensity of the Physiological Properties of the Alkaloids Found in Various Species of Anhalonium.

Species.	*A. fissuratum.*	*A. Williamsii.*	*A. Lewinii.*					
vestigator.	Heffter, 1894.	Heffter, 1894.	Heffter, 1894.			Lewin, 1888.	Lewin, 1894.	
Names of bases reported	Anhalin.	Pellotin.	Alkaloid A.	Alkaloid B.	Alkaloid C.	Anhalonin.	Crystalline anhalonin hydrochlorate.	Amorphous anhalonin hydrochlorate.
Minimum observed active doses.	A cat was given 0.107 gram per kilo of the body weight of anhalin sulphate by hypodemic injection. After a violent attack of vomiting the animal recovered in forty-five minutes. 0.1 gram was without action when taken by way of the mouth by the investigator himself.	For a rabbit, 0.07 gram per kilo: for a cat 0.05 gram per kilo, the alkaloid being dissolved in acidulated water and administered hypodermically. A slight effect is felt by men after taking 0.05 - 0.06 gram by way of the mouth.	No experiments with warm-blooded animals are reported with the alkaloids. The experiments with frogs were rather limited in consequence of an insufficient supply of material.			Several tests with animals were reported, but they were mostly made with preparations that were likely to contain more than one of the alkaloids.	0.01 gram, was found to be active, and 0.02–0.04 gram poisonous in the case of rabbits, but the weights of the animals were not reported.	The poisonous dose for frogs was 0.002 to 0.004 gram: for rabbits, 0.005 gram, 0.01 causing marked tetanus.
			0.02 gram of the sulphate by hypodermic injection was necessary to obtain pronounced symptoms in the case of a frog, (*Rana temporaria.*)	As small a hypodermic dose as 0.005 gram of the sulphate was active in the case of a frog.	0.005 gram of the brown, sirupy mother liquor was sufficient to cause "reflex tetanus" when administered hypodermically to a frog.			
Lethal dose, grams per kilo of body weight	0.05 gram of the sulphate given hypodermically killed a medium-sized frog (*Rana temporaria*) in twenty minutes. The weight of the animal was not stated.	For rabbits, 0.10 of the free base, dissolved in acidulated water and administered hypodermically.					For rabbits, 0.16 - 0.20 administered hypodermically.	For rabbits, 0.06-0.10 administered hypodemically.

The nature of the action.	The action of this alkaloid upon frogs is summed up as a paralysis of the central nervous system without preceding excitement, the action apparently being limited to the brain.	0.05–0.06 gram has a narcotic effect when taken by men. This is evidenced by a feeling of weariness that comes on two hours after taking the drug into the stomach. There is also a heaviness of the eyelids, disinclination to physical and mental exertion, and a lowering of the pulse rate. These symptoms all disappeared after one-half to one hour. In the case of rabbits, large doses produce muscular weakness, followed by tetanic spasm, with opisthotonus, increasing in intensity or followed by recovery according to the amount of the dose. There is increase of reflex excitability and the tetanic spasm can be produced by exterior disturbance. With frogs the tetanic condition may last three or four days.	No increase of reflex excitability was observed.	No increase of reflex excitability was observed.	More active than either "Alkaloid A," "Alkaloid B," or pellotin. Tetanic spasms with increased reflex excitability.		Tremors, tetanic spasms with opisthotonus, marked increase of reflex excitability. In the case of frogs, the animal remains for several days in such a condition that any slight exterior disturbance calls forth a series of tetanic convulsions.	Tetanic spasms, with increase of reflex excitability, the latter apparently being less marked than in the case of the crystalline anhalonin hydrochlorate.



Top. Edge. Under side.

Fig. 1. "Mescal buttons."

To follow page 640).

Fig. 2. *Anhalonium Lewinii.*

Fig. 3. *Anhalonium Williamsii.*

Fig. 4. Anhalonium fissuratum.

Fig. 5. Anhalonium prismaticum.

Fig. 6. Anhalonin hydrochlorate.

Fig. 7. Hydrochlorate of a new alkaloid separated from *Anhalonium Lewinii*. (Enlarged nine diameters.)

The materials used by Lewin in his experiments reported in 1894 were prepared in the laboratory of E. Merck & Co., of Darmstadt. In their report to Lewin, mention was made of the presence of still a third base in the drug, which forms a crystallizable hydrochlorate that is easily soluble in cold water. It seems quite possible that the substance described under the name of "amorphous anhalonin hydrochlorate" was a mixture of alkaloidal hydrochlorates.

Heffter also made a cursory examination of a small sample of *Anhalonium prismaticum* and found it to contain a small percentage of alkaloidal constituents possessing high physiological activity.

In the article published by Lewin, in 1894, and cited above, mention is made of a partial analysis of a sample of *Anhalonium Jourdanianum* made in 1889 with the result of the separation of an alkaloid that formed a crystalline hydrochlorate and resembled anhalonin in its characteristic color-reaction as well as the nature of its physiological action upon frogs. In the same article report is also made of an examination of *Anhalonium Williamsii*, several species of Mammillaria, and one species of *Opuntia*. The study of *A. Williamsii*, which was made in 1891, resulted in the separation of an alkaloid that caused an increase of reflex excitability, and marked tetanus when administered to frogs. The tendency of the tetanic condition to continue for several days was very pronounced. The milky juices yielded by *Mamillaria polythele*, *M. centricirrha* var. *pachythele*, *M. pulchra*, *Haw.* and *M. arietina*, were found to possess no poisonous properties. *Mammillaria uberiformis* was found to be poisonous. *Rhipsalis conferta*, a member of the *Opuntia* group, yielded a slimy juice that was difficultly soluble in water. When this was administered to frogs by hypodermic injection a paralysis of the voluntary muscles was produced, which was followed by heart failure.

It is very apparent from the results of the investigations which I have thus briefly summarized, that the *Cactaceae* is a group of plants worthy the attention of the botanist, the chemist, the pharmacologist, the physician, and the toxicologist, as well as the attention of the entire mass of nature-loving human-

ity. It is to be hoped that American scientists will not leave the task of exploring this promising field entirely to workers beyond the sea, considering our proximity to much of the necessary material.

It is the purpose of the present article to bring the subject to the attention of American investigators and to briefly outline the work that has been done in the laboratory of the U. S. Department of Agriculture. "Mescal buttons," the dried, commercial form of *Anhalonium Lewinii*, have served as the starting point for all our investigations. Fig. 1 shows the appearance of the "buttons" when viewed upon the top, upon the edge, and upon the under side.

Figs. 2, 3, 4, and 5, show the appearance of living specimens of *Anhalonium Lewinii*, *A. Williamsii*, *A. fissuratum*, and *A. prismaticum*, respectively, the illustrations being prepared from photographs made by the author from plants growing in the National Botanical Gardens.

An alkaloid corresponding in its properties to Lewin's anhalonin has been prepared in a considerable amount and in a high state of purity. Fig. 6 shows the appearance of the bottom of a crystallizing dish in which the hydrochlorate was crystallized from alcohol by spontaneous evaporation over sulphuric acid in a vacuum.

A second and, very recently, a third alkaloid have been separated from the drug. All three of these alkaloidal preparations have been subjected to physiological tests by Drs. Prentiss and Morgan, and the results of their investigations will soon be published in the *Medical Record*. They have recently published two articles upon the physiological action and therapeutic value of the crude drug in the *Therapeutic Gazette*.[1] As for the third alkaloid separated, let it suffice to say for the present that it has been found to be much stronger than any alkaloid hitherto separated from any member of the genus Anhalonium, as 0.02—0.025 gram of its hydrochlorate per kilo or body weight is fatal to rabbits, and 0.03 gram per kilo of body weight suffices to kill a full grown guinea-pig. The hydrochlorate of this alkaloid crystallizes in nodular groups of radiating needles. Fig. 7 was made

[1] Sept., *1895*, and Jan., *1896*.

from a photograph of crystals obtained by the spontaneous evaporation of a solution of the alkaloidal salt in ninety per cent. alcohol.

An examination of the resinous constituents of the plant is in progress, as well as a study of those of its constituents that are of interest to the vegetable physiologist rather than to the therapeutist.

A more extended report of this work is reserved for a future paper. Before closing this preliminary announcement, however, I wish to express my indebtedness to Dr. Wiley for much greatly appreciated assistance in the work, and to Dr. Brown for the aid that he very kindly rendered me in the preparation of the photographs used for the illustration of the article. I also desire to express my appreciation of the patience with which both Dr. Wiley and the gentlemen of the Bureau of Ethnology have awaited the progress of this work, which has been largely limited to spare moments not required by other duties.

WASHINGTON, D. C., May 11, 1896.

THE SULPHURIC ACID PROCESS OF REFINING LIXIVIATION SULPHIDES.[1]

BY FREDERIC P. DEWEY.

Received May 21, 1896.

THE time is fast approaching when more chemistry must be used in the extraction of the precious metals in the United States. The chief objections to chemical methods are the technical skill required in the management, the higher grade of labor necessary and the time required to turn out product, thus locking up large amounts of capital; but these difficulties are becoming less applicable all the time. Then too, the wonderful success attained in this country in extracting the precious metals by smelting with lead has retarded the application of chemical methods.

The chemical process of extracting silver by lixiviating, or leaching its ores with solution of hyposulphite of sodium, was introduced by von Patera in 1858, and has been variously improved, notably by the substitution of the calcium salt for

[1] Read before the Washington Section of the American Chemical Society, March 12, 1896.

the sodium salt. This process, however, had some serious disadvantages, the two most important being the necessity for a high degree of chlorination and the recovery of the precious metals in the form of sulphides.

In order to get a satisfactory extraction it was necessary to chlorinate thoroughly, and this was not always possible, especially in the presence of lime. Mr. E. H. Russell discovered, however, that the addition of a copper salt to the hyposulphite of sodium solution, resulting in the formation of a cuprous sodium hyposulphite, largely increased the solvent power of the solution for the ordinary silver minerals in ores, so that it was not necessary to roast with salt so carefully or so thoroughly; or, with equal care in roasting Russell's "Extra Solution," as it is called, will take out more silver than a plain hyposulphite solution. In other words, the use of the double hyposulphite increased the extraction of silver by the leaching process.

The Russell process can be applied to some ores without roasting, but in general the ores are roasted with salt. They are then charged into large vats and leached with water to extract soluble salts; they are then treated with a succession of hyposulphite solutions of varying compositions and strengths, according to the character of the ore, and are finally washed with water to displace the hyposulphite solution. The tailings are then run to waste. The various solutions carrying the precious metals are gathered up in large vats and precipitated with sodium sulphide. This produces a precipitate of sulphides of gold, silver, copper and a little lead. Most of the lead of the solutions is generally precipitated by a previous treatment with sodium carbonate.

The Russell process has also been applied with marked success to the tailings of other processes, such as amalgamation and the old process of lixiviation with plain hyposulphite. Under favorable circumstances, tailings can be lixiviated for $1.50 to $2.00 a ton.

The actual extraction of the silver by the Russell process reaches a high percentage of the total silver present in the ore. In one instance a mill treating nearly 23,000 tons a year averaged nearly ninety-four per cent. for the whole year. With

tailings the extraction is not so high, being from fifty to seventy per cent.

Having brought the extraction of the silver from the ore up to a satisfactory figure there remains the question of dealing with the sulphide precipitate. For a long time this was admittedly the weakest point in the leaching process.

After going through all the operations of crushing, roasting, leaching and precipitating, the best we can say is that we have a rich concentrate, which requires further treatment to convert the precious metals contents into saleable forms.

It is true that these concentrates are often very rich and may even carry a higher silver percentage than the bullion produced by many amalgamating mills, or even by amalgamating the same ores, but the silver, as well as the other metals, are chemically combined with sulphur, and they are also in bad physical condition, being dry powders which are very susceptible to loss in handling, while their sampling and assaying present unusual difficulties.

The improvement in leaching, introduced by the Russell process and the success of this process has stimulated the development of processes for refining the sulphides. In the early days several processes of dealing with the sulphides were proposed and some of them tried more or less, but the business finally settled down to sending the sulphides to the smelters for treatment, although this was well known to be troublesome and expensive. In 1891 Mr. C. A. Stetefelt introduced at the Marsac Mill, Park City, Utah, an unpatented process which was built up out of the general fund of information available. The process consisted in matting the sulphides, grinding, roasting, grinding again and dissolving the copper out in dilute sulphuric acid, then melting the silver and crystallizing the bluestone. It did not yield fine bullion, but the bullion had to be refined as well as parted, besides there was some loss. This process was thoroughly tried at the Marsac Refinery, and then a year's run was made, the net results of which was that it did not prove sufficiently better than sending the sulphides to smelters.

In 1893 the Dewey-Walter Refining Company undertook the refining of the Daly sulphides in the the Marsac Refinery by the

sulphuric acid process, upon which a United States patent has been issued to the writer. Naturally difficulties were encountered in starting a new process and much of 1893 was taken up in getting the process into smooth working order, but in 1894 a run was started in which all the regular sulphides produced by the Marsac Mill in 1894 were refined and thus a complete set of statistics of the operation of the process was obtained.

Broadly speaking the process consists of six main operations:

First. Boiling the sulphides with strong sulphuric acid in an iron pot.

Second. Dissolving out the sulphates of copper and silver in a lead lined tank, leaving a residue containing the gold and lead of the sulphides and also rich in silver.

Third. Precipitating the silver out of the filtered solution by copper plates.

Fourth. Sweetening, drying, pressing and melting the cement silver.

Fifth. Treatment of the solutions after the removal of the silver to crystallize the sulphate of copper and recover the excess of acid for reuse.

Sixth. Treatment of the gold-bearing residues.

The 1894 run of the Marsac Leacher produced 116,519½ pounds of regular sulphides, which were treated by this process. For convenience they were divided into twenty-five lots, mostly from 4,500 to 5,500 pounds in weight. As reported by the assayer of the Daly Mining Company, these lots varied in composition as follows:

COMPOSITION, DALY SULPHIDES FOR 1894.

	Silver. Ounces per ton.	Gold. Ounces per ton.	Copper. Per cent.	Lead. Per cent.
Maximum	11,127	14.8	32.9	0.2
Minimum	7,835	7.6	20.3	0.6
Average	9,827.4	11.225	27.17	0.33

The totals were:

Silver	572,544.4	ounces.
Gold	646.1	"
Copper	31,585.3	pounds.
Lead	385.6	"

THE PLANT.

The plant required is simple and all of it is well known. It is easily managed and no especially skilled labor is required. It consists of two ordinary iron pots, such as are used in parting bullion; a series of twenty-one lead-lined tanks for dissolving, filtering the solutions, precipitating the silver and filtering off and sweetening the cement silver, together with crystallizers to recover the bluestone, and evaporators to concentrate the mother liquors for reuse in the pot; a dryer and press for the cement silver; furnace for melting the bullion; four storage tanks for acid; and pumps for handling the liquids. The large pot for boiling the sulphides is forty-six inches in diameter and three feet deep. It is hung by its rim on a cast iron plate and is enclosed in brick work over a fire-box. It stands fourteen feet from the floor and is provided with a suitable hood and stack to take off the fumes. The smaller pot is used for boiling the residues. The tanks are arranged in steps to allow the descent of the solutions from one to the other by gravity.

THE PROCESS.

The process consists in boiling the sulphides in strong sulphuric acid to convert the sulphides into sulphates. The sulphate of silver is soluble in strong sulphuric acid, but the anhydrous sulphate of copper is practicably insoluble. Owing to the large percentage of copper, averaging twenty-seven per cent. in 1894, in the sulphides a large quantity of insoluble sulphate is produced, and this is one of the most serious difficulties of the process. After boiling the charge is removed to the dissolving tank, in which are put wash water and weak solutions. Here the copper sulphate goes into solution along with the silver. The solution is filtered into the precipitating tanks where the silver is precipitated by metallic copper, after which the solutions are concentrated and go to the crystallizers to recover the bluestone. Periodically the cement silver is removed to the filter, sweetened, dried, pressed and melted. The mother liquors are concentrated, crystallized and the recovered acid finally sent back to the pot. The residue in the dissolving tank is taken out, washed somewhat and reboiled in acid to remove as much as possible of the silver that it contains.

PRACTICAL OBSERVATIONS.

A charge of about 975 pounds is put into the pot in the morning with about 1,000 pounds of 66° acid and thoroughly mixed and the charge heated. At first the reaction is rather violent; sulphur dioxide is copiously evolved and the fumes carry considerable sulphur, which gives them a yellowish color. At this stage a steam jet may be required to increase the draught. After a while the reaction settles down and the normal charge boils quietly until near the end. As soon as the charge gets stiff, more acid, about 100 pounds, is added, until about 3,000 pounds have been added. Toward the end, evaporated acid is used. As the boiling goes forward anhydrous sulphate of copper is formed in large quantities which separate, forming granular masses. This necessitates frequent stirring of the charge and this in turn is hard on the pots. A net-work of cracks develops and finally the acid finds its way through, when the pot must be replaced. In the 1894 run nine pots were used, two of which were short-lived. Better results have been obtained since.

The progress of the operation can be watched by taking out a small sample of the charge, treating with water and adding hydrochloric acid to the solution ; but this is not necessary after getting familiar with the process, since the color changes from black to brown or dark gray. About ninety per cent. of the total acid used is added before the charge begins to show soluble silver salts. Then the charge foams violently and must be constantly stirred while the fire must be lowered. In about an hour the foaming is over and the charge is finished. This usually occurs in the afternoon of the day after starting. On the second morning the charge is warmed up, generally with the addition of some acid and, as it is rather thick, it is ladled out into a trough which delivers it to the dissolving tank. The pot is then started on a new charge.

The dissolving tank is filled with cold water within six or eight inches and tightly covered, since the introduction of the charge generates much heat. After the charge is in, the cover is raised and the solution stirred with a paddle and boiled with steam, after which it is settled and drawn into the filters. The

first tankful of solution contains most of the copper. It is run into a small precipitating tank and kept separate from the rest of the solution. The charge now resembles thick white mud and is washed eight or ten times with weak acid solutions to remove the silver, after which the residue is thrown into a filter. This residue varies very much, running from 5,000 to 19,000 ounces silver per ton and fifty to 100 ounces gold, the balance being mainly sulphate of lead.

The filters are three to four inches of clean quartz sand on a foundation of lead plates, cocoa matting and asbestos cloth, resting on lead strips, giving a space below. It is impracticable to settle all the very fine residue in the dissolving tank, so some of it passes over into the filters and chokes them up. In about two weeks the filters must be washed by a stream of water from below and the muddy water pumped off the top.

The solution has a reducing action and immediately a separation of metallic silver begins in the dissolving tank, often with the formation of beautiful growths upon the surface of the liquid, and this reaction continues in the filters. By this reaction metallic silver is found in the first residue and some 10,000 ounces may accumulate in the filters during a year's run.

From the filters the solution goes to the precipitating tanks, where the silver is precipitated by copper, cathode plates from an electrolytic refinery being used. The first or copper solutions require a long time to precipitate, sometimes eighteen hours, but ordinary solution is precipitated in four to five hours. During precipitation the solution is stirred by air and heated by steam. When the precipitating tank is cold and the hot solution of silver sulphate runs in, there may be a separation of silver sulphate which may go into the solution again as the solution is heated up, but some of it may also remain with the cement silver and be removed in washing the silver, in which case the wash water must be treated with copper.

When about 20,000 ounces of cement silver have accumulated in the precipitating tanks, it is removed to the sweetening tank and washed with hot water and then with acidulated hot water until the ammonia test shows no copper, which takes about fif-

teen hours. The wash water runs through a guard tank containing scrap iron and then to waste.

The sweetened silver is put into sheet iron pans and dried about twenty-four hours in a steam dryer, pressed into cakes, dried again and melted. In 1894 the melting was done in crucibles holding about 2,400 ounces, or two bars, and about a pound and a half each of borax and niter were used to a crucible. The melted silver was poured into heated and greased light cast steel moulds. After pouring a little sugar was thrown on the liquid silver and the mould covered by a tight fitting cast iron cover. This gives a very smooth surface to the bar. When cool the bars are hammered up and marked. The average fineness for 1894 was 999.4 silver with no gold, 446 bars were shipped, of which 401 were 999.5 fine and forty-five were 999.0 fine.

The bluestone solutions are concentrated to about 35° to 37° B, and run into ordinary crystallizers provided with lead strips and allowed to stand two days or more, when it is pumped back to the evaporators and run up to 42° B. It goes back to the crystallizers, and a crop of crystals containing iron and but little bluestone is obtained. The solution goes back to the evaporator. The crystallizers are filled with cold water, which dissolves most of the iron and only a little of the copper. This solution goes through the guard tank to waste. These bluestone crystals are very small, but answer well in the leacher in preparing extra solution. The mother liquid is brought up to 50°–52° B. and then allowed to stand in a crystallizer several days to separate iron. It is then pumped to storage tanks for use in the pot. While concentrating, considerable iron separates in the evaporators. Periodically this is washed out and the solution run to waste through the guard tank.

After boiling five charges of sulphides, about 750 pounds of wet residue are obtained. This is put into the pot and boiled with a little more than its own weight of acid, after which it is washed and the final residue dried. This residue is very complex in composition, although it is mainly sulphates of silver and lead. There appears to be some acid sulphate, for the sulphuric acid present is far more than sufficient to form normal sulphates, and

yet the sample is so dry that the excess of acid cannot all be free. It contains the gold of the sulphides. During 1894 this residue was shipped away to the smelters for treatment, but at the present time it is being melted on a hearth.

SUPPLIES.

Sulphuric acid is received at the refinery in iron tank cars holding 40,000 to 50,000 pounds. It is stored in two lead-lined wooden tanks and is elevated by a mountejus to two iron receivers above the level of the pots from which it is drawn to feed the pots. In the 1894 run 389,439 pounds were used, being an average of 3.34 pounds per pound of sulphides treated, or 0.68 pound per ounce of silver. Copper to precipitate the silver is used in the form of cathode plates, and 16,832.5 pounds were used, one pound of copper precipitating 2.27 pounds of silver, or 33.1 troy ounces. The ordinary local coal is used and 159,000 pounds were used in the 1894 run. The regular labor required was a superintendent and two men, with an extra man to assist the superintendent in melting bullion. Occasionally some extra labor was required, particularly in shipping residue and making the annual clean-up. Mechanics were also required for special work occasionally, but the lead burning was done by one of the regular men.

RETURNS.

It is a well known fact that, in assaying, some of the precious metals pass into the slag, and some are absorbed by the cupel, causing a loss in the determination. In the case of ordinary ores, this quantity per ton is generally small, although the percentage of the total silver is large. In the case of rich materials, however, the percentage is low and the actual quantity per ton becomes considerable, and when the rich material carries copper the loss of silver per ton becomes quite respectable. In our business transactions, the sulphides are always settled for upon an assay corrected for slag and cupel absorption, which shows from 100 to 200 or even more ounces per ton more than ordinary uncorrected assay shows. Even on the corrected assay the actual amount of silver returned by the refinery on the year's work was 2,078.81 ounces more than the assays called for, show-

ing very plainly that even the corrected assays do not show all the silver really present. This silver was divided as follows:

116,519.5 pounds sulphides contained 572,544.45 fine ounces of silver.

PRODUCT RETURNED.

	Fine ounces silver.	Per cent. total silver.
Fine bullion, free from gold	551,329.89	96.29
Residue	15,773.41	2.79
Cleanings	5,328.87	0.93
On hand	2,191.09	0.38
Total	574,623.26	100.36
Plus clean-up	2,078.81	0.36

All weights of sulphides and products, excepting one covering less than 200 ounces, and all the assays are the originals made by the Daly Mining Company.

It is regarded as an extraordinary showing for a chemical process on the large scale to recover more than the best assay possible calls for.

As to the recovery of gold, I cannot see any reason why it should not equal the silver recovery, but the figures upon the point are not satisfactory. The actual return of gold for the year was 606.9 ounces. The original assay of the Daly Mining Company called for 654.8 ounces, but their re-assay on some of the samples reduced this to 646.1. This left an apparent shortage in the returns of 39.2 ounces. The same samples were assayed by Mr. Charles Earl under my directions, and while the silver result showed a satisfactory agreement with the Daly assays, yet his gold determinations called for only 602.9 ounces, showing a plus clean-up on the year's work of four ounces. After the close of the year's business a general sample was prepared by taking proportionate weights of each of the check samples of the twenty-five lots, and the Daly Co.'s assay of this sample called for 605.9 ounces, and showed a plus clean-up of one ounce. Mr. Earl is no longer with me, so I cannot add his figures on this sample. There are especial difficulties in determining such small quantities of gold in the presence of so much silver.

The conditions of the process are such that I do not see how we could gain so much on the silver and lose on the gold, so that I am satisfied that the process practically recovers all the gold that goes into the operations, although the assays may not always show this.

The bluestone produced amounts to 175,809 pounds, or 3.63 pounds per pound of copper, including the copper in the sulphides and the copper used to precipitate the silver. About 125,000 pounds of bluestone were used by the leacher in preparing extra solution, leaving 50,000 pounds to be sold to outside parties. No particular care is taken to prepare fine large crystals of bluestone, and it is not necessary to purify the solutions from iron except as above described. Most of the bluestone produced goes to the leacher and the size of the crystals is of no moment whatever, while the small amount of iron present does no harm. The best grade showed 0.34 per cent. of protoxide of iron, the medium 0.69 per cent., and the worst, of which only a small quantity was produced, 3.89 per cent.

THE FOLLOWING TABLE SUMMERIZES THE STATISTICS FOR THE YEAR BY THE DEWEY-WALTER PROCESS OF BOILING RUSSELL SULPHIDES IN STRONG SULPHURIC ACID.

First charge of 1894 sulphides to pot, February 20, 1894.
" " " 1895 " " " February 27, 1895.
Sulphides treated, 116,519.5 pounds.
" contained silver by corrected assay, 572,544.45 ounces.
" " copper, 31,585.3 pounds.
" " lead, 385.6 pounds.
" " silver average ounces per ton, 9,827.44.
" " copper average per cent., 27.1 per cent.
" " lead average per cent., 0.33 per cent.
Acid used, 389,439 pounds.
" " per pound sulphides, 3.34 pounds.
" " per ounce silver, 0.68 pound.
Coal, 159,000 pounds.
Copper used to precipitate silver, 16,832.5 pounds.
Total copper, 48,417.8 pounds.
One pound copper precipitated silver, 2.27 pounds.
Bluestone produced, 175,809 pounds.
" " per pound copper, 3.63 pounds.
Regular labor, superintendent and two men.

Extra labor, one man at bullion melting to assist superintendent, laborers for clean-up and shipping residue, etc., mechanics for special work occasionally.

136,519.5 pounds sulphides contained 572,544:45 fine ounces of silver.

PRODUCT RETURNED.

	Fine ounces silver.	Per cent. total silver.
Fine bullion, free from gold	551,329.89	96.29
Residue	15,773.41	2.76
Cleanings	5,328.87	0.93
On hand	2,191.09	0.38
Total	574,623.26	100.36
Plus clean-up	2,078.81	0.36

All weights of sulphides and products, excepting one covering less than 200 ouuces, and all the assays are the originals made by the Daly Mining Company.

The advantages of this process are the phenomenal percentage of silver recovered, and that it is an entirely liquid one from beginning to end, so that there is no loss from handling dry products. There is no roasting to cause loss. A large percentage of the silver is recovered as very fine bars, ready to enter the market. It is so simple and so easily carried out, and the plant is so small and inexpensive that it can be installed at individual leaching works.

Finally, the cost of operating is small; in fact, the value of the bluestone recovered returns a large proportion of the operating expenses.

NOTES ON THE ELECTROLYTIC DETERMINATION OF IRON, NICKEL AND ZINC.

BY H. H. NICHOLSON AND S. AVERY.

Received May 15, 1896.

THE experimental part of this work was undertaken in the spring of 1892. During the progress of the work various articles on the electrolytic deportment of these metals have been published. Some of these investigations are closely related to those carried out by us. As, however, they differ in some important particulars and as some observations have been made which, so far as we are aware, have not as yet been reported, it

seemed well to present the results obtained although some parts of the work are still incomplete.

In the method of manipulation, free use was made of the text-books of Classen and of Smith. A number of cells of the Grove-Tyndall form furnished the current. The current was controlled by means of a rheostat-box. The amperage was determined by means of a "Weston" volt-meter. The metals were deposited in platinum dishes of 300 cc. capacity.

In no case was any attempt made to separate metals by careful regulation of the voltage as the practical utility of such methods may be doubted till the literature of the subject is more copious.

I. THE ELECTROLYTIC DEPORTMENT OF IRON.

The method of Classen and V. Reiss[1] for the determination of the metals in their double oxalate solutions, a method which gives such admirable results in most determinations, cannot be applied with the same degree of convenience to iron, as a strong, current and a hot solution are necessary.

Smith and Muir[2] found that iron is very readily precipitated from ammonium tartrate solutions containing free ammonia. They found, however, that under such circumstances the iron contains carbon. Still tartrate solutions seemed to offer possibilities for quantitative determinations sufficient to warrant a fuller investigation of the subject.

Six grams of tartaric acid was dissolved in water and added to a solution of ferrous sulphate. The solution was then diluted to 150 cc. and rendered strongly alkaline with ammonia. The solution was then placed in a platinum dish, submitted to the action of a current of 0.115 ampere and four volts for six hours.

Taken 0.0477 gram iron. Weight found 0.0476 gram iron.

After weighing, the precipitate was dissolved in dilute sulphuric acid. A trace of the odor of hydrocarbons was present. The solution was then oxidized; precipitated with ammonia and determined in the usual gravimetric way. The weight of the iron oxide corresponded to 0.0465 gram of iron. The carbon present evidently compensated for the weight of the unprecipitated iron.

[1] *Ber. d. chem. Ges.*, 14, 1622.
[2] *J. Anal. Chem.*, 5, 488.

The following determinations were made in a similar manner:

No.	Current amperes.	Time. Hours.	Solution.	Iron taken. Gram.	Weight found. Gram.	Carbon by difference. Gram.
1	0.185	4	Strongly alkaline.	0.0620	0.0418	....
2	0.115	14	Strongly alkaline.	0.0476	0.0487	0.0011
3	0.115	6	Slightly alkaline.	0.0291	0.0294	0.0003
4	0.5	5	Strongly alkaline.	0.0476	0.0492	0.0018
5	0.5	5	Strongly alkaline.	0.0351	0.0364	0.0013

These figures show that strong currents and free ammonia are favorable to the precipitation of carbon. Hence attention was turned to the electrolysis of iron in neutral ammonium tartrate solutions.

To twenty-five cc. of an iron sulphate solution, sodium hydroxide was added till the greater part of the iron was precipitated. A dilute solution of tartaric acid was now added till the greater part of the precipitate was dissolved; five grams of ammonium tartrate were added and the whole diluted to 150 cc. The solution made up in this way was found to be exactly neutral to litmus. It was necessary to employ a stronger current than when free ammonia was present. The following determinations were made:

No.	Current. Amperes.	Time. Hours.	Iron taken. Grams.	Weight found. Grams.	Iron calculated from Fe_2O_3. Grams.
1	0.4	6	0.0630	0.0634	....
2	0.4	6	0.0630	0.0635	....
3	0.5	4½	0.0630	0.0626	0.0620

In all cases carbon was detected in the precipitated iron.

Attention was next given to the determinations of iron in sodium tartrate solutions. In some cases free sodium hydroxide was present. The sodium salt conducts the current much better than the ammonium salt. The precipitation of iron proceeds satisfactorily for a time. After a little black spots appear. When a strong current is employed a white precipitate of ferrous carbonate forms on the deposited metal. Currents of two to four volts and of 0.05 to 0.1 amperes were employed to effect the separation of the iron from the solution. Towards the end of the precipitation carbon deposits rapidly. Vortmann,[1] by using

[1] *Chem. Centrbl.*, 1893, 1070.

currents of low voltage and precipitating the iron in fractions on weighed electrodes, seems to have avoided some of the unfavorable conditions above described. However the general deportment of iron in sodium tartrate solutions was so unpromising that the investigation was not carried further in this direction.

The question now presented itself: "Is the precipitation of carbon with iron peculiar to tartrates or may we expect it when other organic compounds are present?"

To answer this question a number of qualitative tests were made by adding to the iron solution before passing the current, solutions of sugar, alcohol, glycerol or of salts of formic, acetic, lactic, citric, succinic or benzoic acids. The currents employed were of the lowest voltage and amperage sufficient to give a deposit of several milligrams in the course of an hour. As ammonium oxalate gives no precipitate of carbon under any circumstances, so far as we are aware, this reagent was used to hold the iron in solution when necessary. The iron was used in the form of ferrous sulphate.

When formates were present in the absence of other organic compounds, no trace of carbon could be detected in the precipitated iron. In all other cases the precipitated iron contained carbon. In the case of citric acid a quantitative determination was made.

A solution of ferrous sulphate containing five grams of citric acid in the form of sodium and potassium salts with a little free acid was submitted for fourteen hours to a current of 0.2 ampere.

Taken 0.0726 gram iron. Weight found 0.0740 gram iron.

The absence of carbon in the case of oxalates and formates is explained by the fact that these compounds break up under the influence of the current giving off all carbon in the form of its highest oxidation product, *i. e.*, carbon dioxide.

In all cases the amount of carbon deposited was increased by the employment of stronger currents, but in no case was it possible to obtain a precipitate free from carbon, except in the case of formates and oxalates, when organic matter was present.

DETERMINATION OF IRON IN SOLUTIONS CONTAINING AMMONIUM OXALATE AND SODIUM BORATE.

We found that a slight modification of Classen's method

greatly facilitated the precipitation of iron. The following gave satisfactory results:

Twenty-five cc. of a solution of ferrous sulphate were taken, five grams of ammonium oxalate were added and brought into solution by the aid of gentle heat. Five cc. of a saturated solution of borax were now added and the entire solution diluted to 150 cc. A current of 0.02 ampere was allowed to act on the cold solution for sixteen hours. Towards the end of the operation the anode became covered with a slight brown coating. A slight brown deposit also appeared on the dish above the iron deposit. The following method was used to dissolve these deposits. Water was added until the surface of the liquid was raised above the brown deposit in the dish. The positive electrode was then brought in contact for a moment with the side of the dish thus short-circuiting the battery and generating considerable heat in the electrodes. This had the effect of liberating and dissolving the brown deposit. The current was allowed to act for half an hour longer when the dish was removed from the circuit, washed, dried and weighed.

The precipitate was perfectly adherent and showed no tendency to oxidize when washed with alcohol and ether. The following is a tabular statement of the results obtained :

No.	Ammonium oxalate. Grams.	Saturated borax solution. cc.	Current. Ampere.	Time. Hours.	Iron taken. Gram.	Iron found. Gram.
1	5	5	0.02	16	0.0938	0.0933
2	5	10	0.02	17	0.0938	0.0935
3	6	10	0.06	4	0.0938	0.0938
4	5	5	0.072	2	0.0938	0.0939
5	6	5	0.125	2	0.0938	0.0938

It will be seen from the above that the presence of borax facilitates the precipitation of iron in ammonium oxalate solutions. The cause of the appearance of the slight brown deposit and the extent to which it might cause an error in results will be investigated later.

II. THE DETERMINATION OF NICKEL.

The determination of nickel presented no difficulties. The greater part of the experiments with iron were performed in an

analogous way with nickel: in no case was carbon deposited with the nickel. When iron and nickel are deposited together as an alloy in the presence of organic compounds the nickel does not prevent the contamination of the precipitate with carbon.

III. DETERMINATION OF ZINC.

Nearly all the published methods for the electrolytic determination of zinc give fairly satisfactory results. The tendency of the metal to be deposited in a spongy condition and the liability to oxidation are the principal difficulties usually encountered.

The tendency to oxidation may be prevented by the presence of formic acid in the solution, which by the liberation of hydrogen with the metal exercises a reducing action.

By the electrolysis of zinc formate in the presence of formic acid Warwick[1] did not succeed in obtaining a complete deposit. The deposit is greatly influenced by the presence of sodium formate in the solution.

To a solution of zinc sulphate three cc. of formic acid were added and the solution partially neutralized with one gram of sodium carbonate. The entire solution was diluted to 150 cc. and placed in a current of 0.02 ampere for three hours.

Taken 0.0611 gram zinc. Found 0.0603 gram zinc.

In a similar manner the following determinations were made:

No.	Formic acid. cc.	Sodium carbonate. Gram.	Current. Ampere.	Time. Hours.	Weight taken.	Weight found.
1	4	1.5	0.125	3	0.0611	0.0612
2	5	1.0	1.000	3	0.0611	0.0611
3	5	1.0	0.050	3	0.0611	0.0611

The deposit adhered well, was compact and evenly distributed on the surface of the dish, the color was light gray, in some cases almost metallic in luster. As will be seen from the figures, a considerable variation in the strength of the current is allowable. This method is not allowable in the presence of the metals of the hydrogen sulphide group, as well as in the presence of iron, nickel and cobalt.

CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA.

[1] *Ztschr. anorg. Chem.*, 1, 291.

CORRESPONDENCE.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., June 5, 1896.

Editor Journal of the American Chemical Society, Easton, Pa.:

DEAR SIR.—I am informed by the Chairman of the Committee of Arrangements of the Second International Congress of Applied Chemistry, that the meetings of the Congress will begin in Paris on the 27th of July, at the Sorbonne, at 10 o'clock A. M. The meetings of the Congress and of the Sections will be continued until the 7th of August.

Chemists intending to present papers should send the titles, without delay, together with the length of time required, to Monsieur F. Dupont, 156 Boulevard de Magenta, Paris, France. Those who intend to be present in person should also inform Monsieur Dupont of that fact.

Respectfully,
H. W. WILEY,
Chairman of American Committee.

BOOKS RECEIVED.

Bulletin No. 43. Composition and Digestibility of Corn Ensilage, Cow Pea Ensilage, Soja Bean Ensilage, and Corn Fodder. University of Illinois, Agricultural Experiment Station, Urbana, Ill. April, 1896. 28 pp.

Special Bulletin. Commercial Fertilizers. Purdue University, Lafayette, Ind. May, 1896. 8 pp.

Bulletin No. 17. Hay Substitutes. Storrs Agricultural Experiment Station, Storrs, Conn. June, 1896. 8 pp.

Bulletin No. 38. (1) General Discussion on Commercial Fertilizers. (2) Analyses of Fertilizing Materials Sent On for Examination. (3) Observations Regarding the Composition of Paris Green. (4) Observations Concerning the Action of Muriate of Potash on the Lime Constituents of the Soil. Hatch Experiment Station of Massachusetts Agricultural College, Amherst, Mass. March, 1896. 16 pp.

Bulletin No. 39. Economic Feeding of Milch Cows. Hatch Experiment Station of Massachusetts Agricultural College, Amherst, Mass. April, 1896. 23 pp.

Bulletin No. 63. Tobacco. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. May, 1896. 20 pp.

Yearbook of the United States Department of Agriculture, 1895. Washington: Government Printing Office. 1896. 656 pp.

VOL. XVIII. [AUGUST, 1896.] No. 8.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

PHOTOMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF LIME AND SULPHURIC ACID.[1]

BY J. I. D. HINDS.

Received May 14, 1896.

THE want of a rapid method of determining with a close approximation the amount of lime and sulphuric acid in drinking water led me to the study of the opacity of fine white precipitates suspended in water. I precipitated in weak solutions lime with ammonium·oxalate, and sulphuric acid with barium chloride, then measured the height of a column of the liquid containing the precipitate through which the flame of a common candle was just invisible. I expected only a rude approximation, but to my surprise, I found that between certain limits, an accuracy is attainable equal to that of the ordinary volumetric methods.

APPARATUS.

The only apparatus needed is a cylinder graduated from the bottom in centimeters and tenths. The cylinder should have a plain polished bottom, like Nessler cylinders, and should have a lip at the top. The one I use was made for me by Eimer and Amend. It is four cm. wide and twenty cm. high. The graduations runs to eighteen cm. This cylinder, however, is not absolutely necessary. A common beaker may be used and the depth of the liquid measured with a small ruler.

[1] The manuscript of this article was sent similtaneously to the Chemical News and to this Journal. Owing to the absence from home of Professor Hinds, his proof was delayed too long to allow of publication of the article in the July issue.

THE METHOD.

For Sulphuric Acid.—To determine the value for sulphuric acid, I used a decinormal solution whose actual strength was one cc. equal to 0.00492 gram sulphuric acid. I took ten cc. of this solution, acidulated it slightly with hydrochloric acid, and diluted it to 200 cc. Of this solution I took forty cc., which contained 0.00984 gram sulphuric acid. To this I added enough solid barium chloride to effect complete precipitation, mixed thoroughly by pouring from beaker to cylinder and back, then measured the depth of the column through which the flame was just invisible. I then added successive portions of ten cc. water, taking the measurement after each addition. The measurement is made as follows: Hold the cylinder some twelve inches above the burning candle; looking downward through the cylinder, pour in the liquid until the image of the flame just disappears, then read the depth of the liquid. By applying the lip of the beaker to the lip of the cylinder, a very gentle stream may be made to flow in. The reading should be made two or three times so as to be sure to read the proper tenth. It is well also to enclose the cylinder in the hand, cutting off the surrounding light, so that the observation may be more accurate.

In this way I obtained the series of determinations given below. The strength of the solutions is expressed in per cent. of sulphuric acid, and is represented by y. Column 1 gives the number of the solution; column 2 the per cent. of sulphuric acid; columns 3, 4, 5 and 6 give the depth of the liquid in centimeters and tenths for four series of observations; column 7 contains the mean of these depths, expressed also by x; column 8 contains the products of these means by the percentage, also represented by xy.

No.	Per cent. sulphuric acid. y.	cm.	cm.	cm.	cm.	cm. x.	xy.
1......	0.0246	2.4	2.4	2.4	2.4	2.4	0.0590
2......	0.0197	3.0	3.0	3.0	3.0	3.0	0.0591
3......	0.0164	3.6	3.6	3.6	3.5	3.575	0.0586
4......	0.0140	4.2	4.2	4.2	4.2	4.2	0.0588
5......	0.0123	4.7	4.7	4.8	4.7	4.75	0.0584
6......	0.0109	5.3	5.4	5.4	5.3	5.35	0.0583

No.	Per cent. sulphuric acid. y.	cm.	cm.	cm.	cm.	cm. x.	xy.
7......	0.0098	5.8	5.9	5.9	5.8	5.85	0.0573
8......	0.0089	6.4	6.4	6.4	6.4	6.4	0.0570
9......	0.0082	6.9	6.9	6.9	6.9	6.9	0.0566
10......	0.0067	7.4	7.5	7.5	7.5	7.475	0.0568
11......	0.0070	8.0	8.0	8.1	8.1	8.05	0.0564
12......	0.0066	8.6	8.6	8.7	8.7	8.65	0.0570

I found that the continued agitation and dilution of the solutions seemed to increase the opacity, though very slightly. I therefore made another series with solutions more dilute with the following results:

No.	Per cent. sulphuric acid. y.	cm.	cm.	cm.	cm.	cm. x.	xy.
1.......	0.0098	6.1	6.1	6.0	6.1	6.075	0.0595
2.......	0.0089	6.6	6.7	6.6	6.6	6.925	0.0589
3.......	0.0083	7.2	7.3	7.3	7.3	7.275	0.0597
4.......	0.0075	7.9	7.9	7.9	7.9	7.9	0.0592
5.......	0.0070	8.5	8.5	8.4	8.4	8.45	0.0591
6.......	0.0066	9.0	9.1	9.1	9.1	9.075	0.0598
7.......	0.0061	9.6	9.6	9.7	9.7	9.675	0.0590
8.......	0.0058	10.2	10.2	10.2	10.2	10.2	0.0591
9.......	0.0055	10.8	10.8	10.8	10.8	10.8	0.0594
Mean value of xy..................................							0.0593
Mean value for xy for first six of first series..........							0.0587
Mean of the two..................................							0.0590

We observe that the product xy, that is, the number obtained by multiplying the per cent. of sulphuric acid in the solution by the depth of the column through which the flame is just invisible, is a constant. The curve, therefore, made by taking the one as the abscissa and the other as the ordinate is an hyperbola referred to its asymptotes, of which the equation is

$$xy = 0.0590.$$

This curve is shown in the accompanying diagram. The abscissas are centimeters and the ordinates are 0.01 per cent. to the centimeter.

Solving the equation for y, we have

$$y = \frac{0.0590}{x}.$$

To find the amount of sulphuric acid in any solution, observe

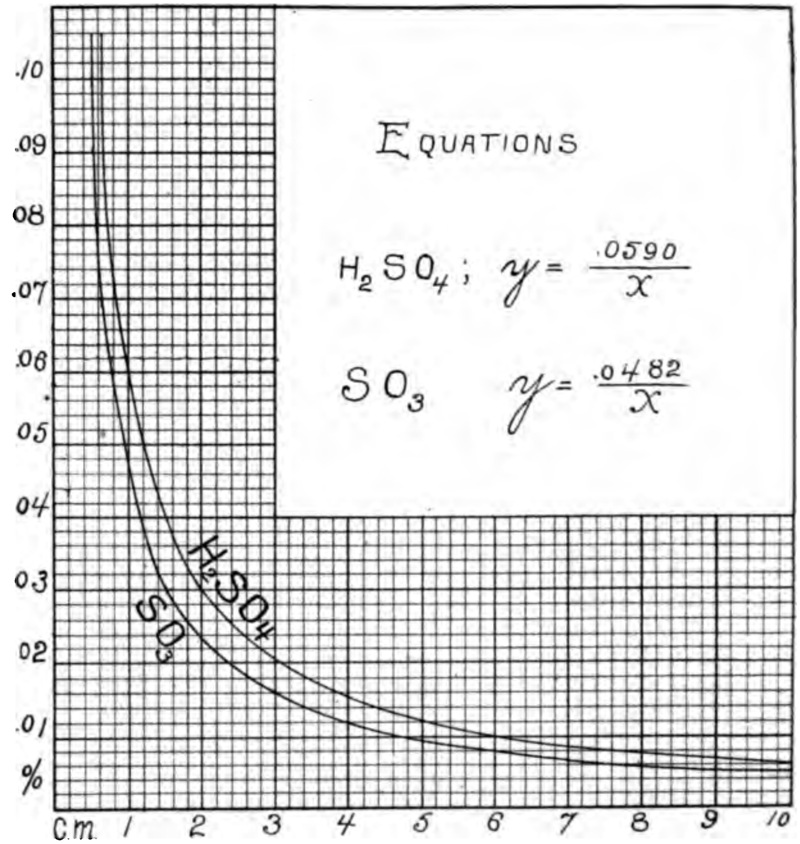


Diagram 1.

the value of x, divide this into 0.0590, the quotient will be the per cent. of sulphuric acid. Remove the decimal point three places to the right, the result will be parts in 100,000. For example, suppose the depth observed is five cm. The quotient is 0.0118. The solution, therefore, contains 0.0118 per cent. of sulphuric acid, or 11.8 parts in 100,000.

For sulphur trioxide the equation is $y = \frac{0.0482}{x}$. This curve is shown in the diagram. In the above example the amount of sulphur trioxide is 0.00965 per cent., or 9.65 parts in 100.000.

PROBABLE ERROR.

To determine the probable difference between the observed and computed values, we may compare the second set of observations above with the percentages computed from the equation. In the following table the first column contains the observed depths of the liquid, the second gives the actual strength of the solutions used, the third gives the numbers calculated from the equation, the fourth contains the difference, and the fifth the square of the difference between the numbers in the two preceding columns. The difference is represented by v.

cm.	Per cent. used.	Per cent. computed.	v.	v^2.
6.0	0.0098	0.0098	0.0000	0.00000000
6.6	0.0089	0.0089	0.0000	0.00000000
7.3	0.0082	0.0081	0.0001	0.00000001
7.9	0.0075	0.0075	0.0000	0.00000000
8.5	0.0070	0.0069	0.0001	0.00000001
9.0	0.0066	0.0065	0.0000	0.00000001
9.7	0.0061	0.0061	0.0000	0.00000000
10.2	0.0058	0.0057	0.0001	0.00000001
10.8	0.0055	0.0055	0.0000	0.00000000
			Sum Σv^2	0.00000004

By the method of least squares, the probable error is expressed in the equation

$$r = 0.6745 \sqrt{\frac{\Sigma v^2}{n-q}},$$

in which $n =$ the number of observations, in this case 9, and q the number of constants in the equation, in this case 1. Making the substitutions, the value becomes

$$r = 0.6745 \sqrt{\frac{0.00000004}{8}} = 0.00005.$$

The probable difference then between an observed and a computed value is 0.00005 per cent., or one part in 2,000,000.

For Calcium Carbonate.—In the investigation of lime I used a solution of calcium chloride whose strength corresponded exactly to 0.001 gram of calcium carbonate to the cubic centimeter. Ten cc. of this solution was taken and diluted with twenty cc. of water, then enough solid ammonium oxalate was added to pre-

cipitate the whole of the calcium. The solution was then poured into the photometric cylinder and the depth measured as in the case of sulphuric acid. Portions of ten or twenty cc. of water were successively added and the depth observed after each addition. The results are given in the following table. In column 1 is the number of the solution; column 2 shows the per cent. of calcium carbonate; columns 3, 4, 5, 6, and 7 contain the measured depths of the liquid at which the flame became invisible; column 8 contains the means of these depths, and column 9 the product of these means by the per cents. in column 2, represented as before by xy. The three determinations in the fifth series were made simply as a check. Many other independent determinations were made in order to ascertain whether there was a change of opacity, and whether the precipitation would be different in the weaker solutions. No material difference was found.

No.	Per cent. calcium carbonate.	cm.	cm.	cm.	cm.	cm.	x.	xy.
1	0.0333	2.1	2.3	2.3	2.4		2.250	0.0750
2	0.0250	2.8	2.9	2.9	2.9		2.875	0.0718
3	0.0100	3.5	3.6	3.5	3.5		3.525	0.0705
4	0.0167	4.1	4.2	4.1	4.1	4.2	4.14	0.0691
5	0.0143	4.7	4.8	4.7	4.7		4.725	0.0676
6	0.0125	5.3	5.5	5.3	5.3		5.35	0.0669
7	0.0111	6.0	6.1	5.9	6.0		6.0	0.0666
8	0.0100	6.6	6.8	6.6	6.7		6.675	0.0668
9	0.0091	7.3	7.4	7.3	7.4	7.4	7.36	0.0670
10	0.0083	8.0	8.0	8.0	8.1		8.03	0.0666
11	0.0077	8.8	8.6	8.6	8.8		8.7	0.0670
12	0.0071	9.5	9.3	9.3	9.5		9.4	0.0667
13	0.0067	10.2	0.9	9.9	10.1	9.9	10.0	0.0670

Examining the values of xy, we find that they are not constant. They diminish rapidly at first, then more slowly. The equation is, therefore, not so simple as in the case of sulphuric acid. It appears, however, to be an hyperbola, and we may assume that its equation has the form

$$xy + by = a,$$

in which b and a are constants whose values are to be determined. Substituting the values of x and y from the above table,

we obtain thirteen observation equations. The values of a and b are then found according to the method of least squares by forming and solving the two sets of normal equations. The first set will be the same as the observation equations; the second set is obtained by multiplying each equation by its cofficient of b. These equations are as follows:

$$
\begin{array}{ll}
0.0750 + 0.0333\,b = a & 0.002500 + 0.001111\,b = 0.0333\,a \\
0.0718 + 0.0250\,b = a & 0.001795 + 0.000625\,b = 0.0250\,a \\
0.0705 + 0.0200\,b = a & 0.001410 + 0.000400\,b = 0.0200\,a \\
0.0691 + 0.0167\,b = a & 0.001151 + 0.000271\,b = 0.0167\,a \\
0.0676 + 0.0143\,b = a & 0.000967 + 0.000204\,b = 0.0143\,a \\
0.0669 + 0.0125\,b = a & 0.000836 + 0.000156\,b = 0.0125\,a \\
0.0666 + 0.0111\,b = a & 0.000740 + 0.000124\,b = 0.0111\,a \\
0.0668 + 0.0100\,b = a & 0.000668 + 0.000100\,b = 0.0100\,a \\
0.0670 + 0.0091\,b = a & 0.000610 + 0.000083\,b = 0.0091\,a \\
0.0666 + 0.0083\,b = a & 0.000553 + 0.000069\,b = 0.0083\,a \\
0.0670 + 0.0077\,b = a & 0.000516 + 0.000059\,b = 0.0077\,a \\
0.0667 + 0.0071\,b = a & 0.000474 + 0.000050\,b = 0.0071\,a \\
0.0670 + 0.0067\,b = a & 0.000449 + 0.000045\,b = 0.0067\,a
\end{array}
$$

Adding the equations together, we have

$$0.8886 + 0.1818b = 13a. \quad 0.012668 + 0.003304b = 0.1818a.$$

Dividing by the coefficient of a and eliminating, we have

$$a = 0.0642 \qquad b = -0.3$$

The required equation is therefore

$$xy - 0.3\,b = 0.0642,$$

or, solving for y

$$y = \frac{0.0642}{x - 0.3}.$$

For the per cent of CaO the equation is

$$y = \frac{0.0360}{x - 0.3}.$$

This is the equation of an hyperbola referred to one of its asymptotes as the axis of x and to an axis of y three-tenths cm. to the left of the other asymptote. The abscissas are centimeters and the ordinates are 0.01 per cent. to the cm. The curves are shown in the accompanying diagram.

As an example, let us suppose that the observed depth is four and seven-tenths cm. Subtract 0.3 and divide 0.0642 by the

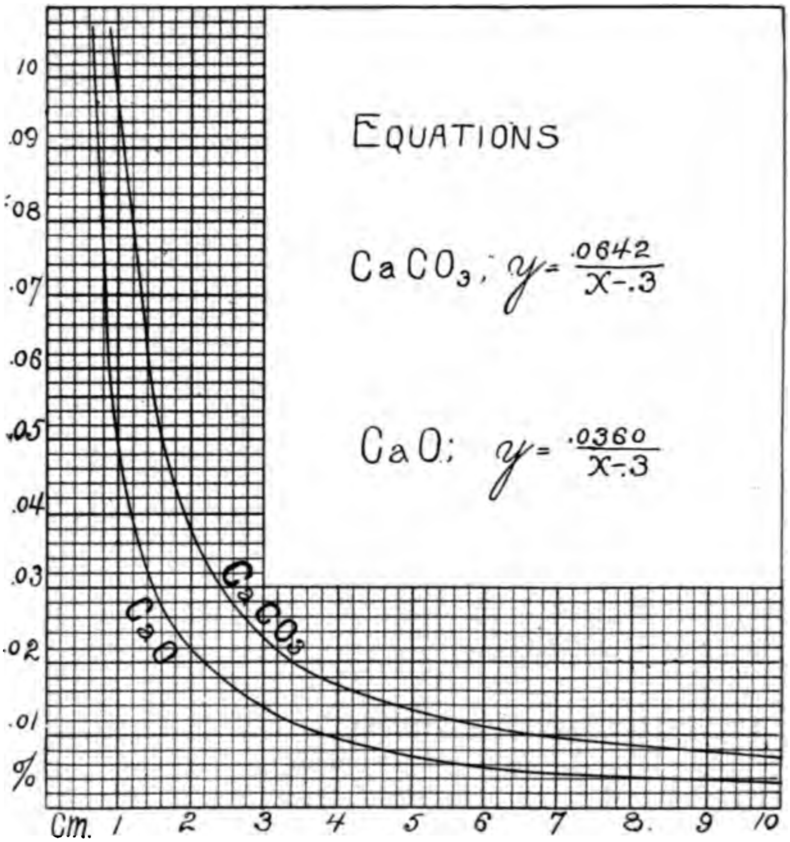


Diagram 2.

remainder. The quotient 0.0146 is the per cent. of calcium carbonate. Dividing this by 1000 we have 14.6 parts to the 100,000.

PROBABLE ERROR.

To determine the probable error of an observation we may compare as before the numbers found by observation with those computed from the equation, as follows :

x.	Strength used.	Strength computed.	v.	v^2.
2.9	0.0250	0.0247	0.0003	0.00000009
3.5	0.0200	0.0201	0.0001	0.00000001
4.1	0.0167	0.0170	0.0003	0.00000009

x.	Strength. used.	Strength. computed.	v.	v^2.
4.7	0.0143	0.0146	0.0003	0.00000009
5.35	0.0125	0.0127	0.0002	0.00000004
6.0	0.0111	0.0112	0.0001	0.00000001
6.7	0.0100	0.0100	0.0000	0.00000000
7.4	0.0091	0.0091	0.0000	0.00000000
8.0	0.0083	0.0085	0.0002	0.00000004
8.7	0.0077	0.0077	0.0000	0.00000000
9.4	0.0071	0.0071	0.0000	0.00000000
10.0	0.0067	0.0066	0.0001	0.00000901
			Sum Σv^2	0.00000038

Using the same value for error as before, in which in this case n, the number of observations, is 12, and q, the number of constants in the equation is 2, we have

$$r = 0.6745\sqrt{\frac{0.00000038}{12-2}} = 0.00013 \text{ per cent.}$$

That is, the probable difference between an observed and computed strength of a solution is 0.00013 per cent., or thirteen parts in ten million.

SOURCES OF ERROR.

The principal sources of error in this method are two. In the first place a light of constant intensity should be used. It makes but little difference what the light is, so it is the same as that with which the constant in the equation is determined. I employed the flame of an ordinary candle as the most convenient. A brighter and steadier light would give better results. Any change of light will of course change the constants.

The second source of error is the personal equation. Each individual can determine this for himself. The error dependent upon the eye can be almost eliminated by using it in the usual way, that is with or without glasses.

Any one can obtain the constants for himself by making a few determination with solutions of known strength. The best strength to use is that between 0.01 and 0.03 per cent. Great care must be used in measuring. If ten cc. of a decinormal solution are taken, a difference of one drop in the measurement may make an error ten times as great as that involved in the method.

PRACTICAL APPLICATION.

I have so far used the method and tested it only in sanitary water analysis and in the analysis of urine. To the water analyst it will be of great value. It gives the lime and sulphuric acid with almost the accuracy of the gravimetric method. It is more accurate than the soap test and is but slightly affected by the presence of magnesium salts.

For determining the sulphuric acid in urine I have found it quite satisfactory. The urine has to be diluted with nine volumes of water and then the color does not sensibly affect the determination.

I see no reason why this method may not be successfully used with all fine white precipitates. It is not suitable for precipitates that settle rapidly or gather quickly into flakes. Whether colored precipitates may be determined in this way is still to be investigated.

I desire to acknowledge obligation to Professor A. H. Buchanan for assistance in determining the equations and probable errors.

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[CONTRIBUTIONS FROM JOHN HARRISON LABORATORY OF CHEMISTRY. No. 12.]

THE SEPARATION OF TRIMETHYLAMINE FROM AMMONIA.

BY HERMANN FLECK.

Received May 8, 1896.

THE quantitative estimation of trimethylamine in presence of ammonia is, I believe not mentioned in the literature, although a number of publications have appeared in which the detection of trimethylamine, in presence of ammonia, by means of the different solubilities of their hydrochlorides in absolute alcohol, has been successfully carried out.

Dessaignes[1] prepared and analyzed with good results the platinum double salt of trimethylamine, by conducting the mixture of ammonia and trimethylamine vapors into hydrochloric acid, evaporating to dryness, extracting with absolute alcohol, precipitating with platinic chloride and recrystallizing the precipitate formed several times from hot water.

[1] *Ann. Chem.* (Liebig), 81, 106.

Wicke[1] adopts the same method, using, however, alcohol-ether extract.

Winkeles,[2] in using this method, further states that while ammonium chloride is soluble to some extent in absolute alcohol, it is rendered totally insoluble by the presence of salts of such bases as trimethylamine.

Eisenberg,[3] by a similar procedure, obtained the platinum double salt in crystals of great purity and perfection.

The success in each case is undoubtedly due to the fact that large quantities of hydrochlorides were used. Winkeles,[4] for example, employed the hydrochlorides obtained from twenty-six gallons of herring brine. Further the mixtures were very rich in trimethylamine.

This method applied to a substance containing a low percentage of the latter yielded results, which clearly show that trimethylamine hydrochloride does not render ammonium chloride insoluble in absolute alcohol, and further does not serve as a good means of qualitative, much less of quantitative, separation. A portion of the mixture containing trimethylamine and ammonia was saturated with hydrochloric acid, evaporated to dryness and extracted several times with portions of several times the volume of boiling absolute alcohol. The alcoholic extract evaporated to dryness gave eighteen per cent. of supposed trimethylamine hydrochloride. To identify the latter, the residue was taken up with alcohol and platinic chloride added. The precipitate formed was redissolved in boiling water and the different fractional crystallizations, consisting of octahedra, analyzed.

	Pt found.	Required for
First crystallization	43.6	$(NH_4Cl)_2PtCl_4$, 43.84
Last "	39.5	Corresponding to a mixture of $2\left((NH_4Cl)_2PtCl_4\right) + 3\left(N(CH_3)_3.HCl\right)_2PtCl_4$, which require 39.4 per cent. Pt.

[1] *Ann. Chem.* (Liebig), 91, 121.
[2] *Ann. Chem.* (Liebig), 93, 321.
[3] *Ber. d. chem. Ges.*, *1880*, 1669.
[4] *Loc. cit.*

Intermediate crystallizations gave intermediate, gradually decreasing results, showing that the isomorphous forms of the two salts crystallized together.

Duvillier, Buisine[1] extract the mixed *sulphates* to prepare pure trimethylamine from the technical product. The suggestion led to the use of the following method which yielded satisfactory results.

The mixed hydrochlorides are repeatedly extracted with portions of a total of five or six times the volume of boiling absolute alcohol and the solvent distilled off in a three-quarter liter distilling bulb. An excess of caustic soda is added to the residue and the gases formed on boiling driven over into a large quantity of water. Litmus is added, followed by the exact quantity of dilute sulphuric acid required to neutralize. The liquid is evaporated to dryness and extracted with one liter cold absolute alcohol, in which trimethylamine sulphate dissolves, leaving ammonium sulphate undissolved. The alcohol is distilled off, the residue transferred to a weighed dish, dried and weighed. In this manner 32,910 grams of the carefully dried mixed chlorides gave two and five-tenths grams trimethylamine sulphate, corresponding to 2.21 grams hydrochloride, or 6.71 per cent.

That the extraction was complete is evident from the total absence of the fishy odor when the extracted residues are treated with alkali. That the extracted material is pure is shown by the following analyses of the octahedral crystals of the platinum double salt prepared from the trimethylamine sulphate:

	Per cent. Pt.	Required for $[N(CH_3)_3.HCl]_2.PtCl_4$. Per cent. Pt.
I. 0.0983 gram gave	36.92	....
II. 0.3017 " "	37.12	36.93

[1] *Ann. Chem.*, (Liebig) (5) 23, 299.

ZIRCONIUM TETRAIODIDE.

By L. M. Dennis and A. E. Spencer.

Received June 9, 1896.

WITH the exception of the tetraiodide all of the normal halides of zirconium have been prepared and described, the fluoride, chloride, and bromide being white, crystalline, sublimable solids.

A few attempts to make the iodide are recorded in the journals, but in no case was the normal compound, zirconium tetraiodide, ZrI_4, obtained. Melliss[1] passed the vapor of iodine over a glowing mixture of zirconia and carbon; he also treated zirconium tetrabromide with potassium iodide, but in neither case did zirconium tetrachloride result. Hinsberg[2] added an aqueous solution of barium iodide to a solution of zirconium sulphate, filtered off the barium sulphate, and evaporated the filtrate over concentrated sulphuric acid. He obtained a compound of the formula $Zr_2I_2O_3$, or $ZrI(OH)_3$. He also passed the vapor of iodine over a heated mixture of zirconium dioxide and carbon and states that no reaction whatever took place. Bailey[3] states that "zirconium[4] is acted upon by chlorine and bromine, in which, on gentle heating, it undergoes vivid combustion, forming the tetrahaloid derivatives, and this is, indeed, a convenient method for obtaining these bodies. The iodide could not be obtained."

In the work here to be described, the authors first attempted to prepare zirconium tetraiodide by passing the vapor of iodine over heated zirconium. The zirconium first used was made by reducing zirconium dioxide with magnesium powder, the two substances being mixed in the proportion employed by Winkler[5] and demanded by the equation

$$ZrO_2 + 2Mg = Zr + 2MgO.$$

This mixture was heated in hydrogen in the usual manner and the resulting black powder was removed from the boat, thoroughly ground, and again heated in hydrogen to insure

1 *Ztschr. Chem.*, *1870*. 296: *Jsb.*, *1870*, 328.

2 *Ann. Chem.* (Liebig), 239, 253.

3 *Chem News.*, 60, 8.

4 Prepared by the reduction of zirconia with magnesium powder.

5 *Ber. d. chem. Ges.*, 23, 2664; 24, 888.

conplete reduction. To free it from magnesia, the product was treated with a saturated solution of ammonium chloride. During this treatment a gas of very disagreeable odor was evolved. It is doubtless similar to that observed by Winkler at this point. The powder was then warmed with dilute twelve per cent. hydrochloric acid and, after collecting it on a filter, it was washed with water containing hydrochloric acid, then with alcohol and ether, and finally was dried in a current of hydrogen. The analysis gave

	Per cent.
Zirconium	80.670
Silicon	0.807
Magnesium	0.117
Hydrogen	0.362
Oxygen (diff.)	18.044
	100.000

These results agree quite closely with those obtained by Winkler,[1] and indicate that the product of the reduction is chiefly zirconium monoxide rather than zirconium.

Although the powder probably contained but very little free zirconium, it was nevertheless heated in hydrogen and vapor of iodine was passed over it. An examination of the product gave no satisfactory indications, however, that an iodide of zirconium had been formed.

Inasmuch as the failure to obtain union between the zirconium and iodine might reasonably be ascribed to absence of free zirconium in the above product, it seemed advisable, before attempting any modification of the iodine treatment, to prepare zirconium by some other method and especially by some procedure in which the presence of any appreciable amount of oxygen is avoided. Under the circumstances the method of Berzelius,[2] the reduction of potassium fluozirconate with metallic potassium, seemed the most promising and was therefore employed.

The potassium fluozirconate was prepared from zircon. The zircon was finely ground, sifted through bolting cloth, and digested with concentrated hydrochloric acid until the acid gave

1 *Ber. d. chem. Ges.*, 23, 2667.
2 *Ann. der Phys.* (Pogg), 4, 117.

no reaction for iron. The powdered zircon, which was now almost perfectly white, was dried and mixed with four times its weight of sodium carbonate. The mixture was fused in an assay crucible furnace, allowed to cool, pulverized, and repeatedly extracted with water. The residue, consisting of zirconia and unattacked zircon together with some silica and ferric oxide, was heated with concentrated hydrochloric acid, evaporated to dryness, and heated in an air-bath to 120° to render the silica insoluble. The dried mass was treated with a little hydrochloric acid, water was added, and the silica and other insoluble matter was filtered off. The filtrate, now containing zirconium chloride and some ferric chloride, was largely diluted with water, and ammonium hydroxide was added until there was formed a slight but permanent precipitate which was then dissolved by adding as little hydrochloric acid as possible. Sulphur dioxide was then passed into the solution until the liquid smelled strongly of the gas. In many cases a precipitate of basic zirconium sulphite formed at once, but, as the compound seemed to be somewhat soluble in an excess of sulphurous acid, the solution was always boiled for from ten to fifteen minutes to insure complete precipitation. In the reaction free hydrochloric acid is formed both by the conversion of the zirconium chloride into the basic sulphite and by the reductfon of the ferric chloride to the ferrous salt. As this acid would dissolve the zirconium sulphite, it was partially neutralized by the addition, from time to time, of a few drops of dilute ammonium hydroxide. The zirconium precipitate not being wholly free from iron, it was dissolved in hydrochloric acid and again precipitated with sulphur dioxide. The pure zirconium basic sulphite thus obtained was dissolved in hydrochloric acid and zirconium hydroxide was precipitated by adding ammonium hydroxide. The well-washed hydroxide was dissolved in hydrofluoric acid, potassium fluoride was added, and the resulting potassium fluozirconate was dissolved in hot water and recrystallized.

The potassium fluozirconate thus prepared was reduced with metallic sodium, the operation being carried out in a cast-iron crucible. The crucible is cylindrical in form with an internal diameter of two inches and depth of five inches. The wall and

bottom are over one inch in thickness. At the top it has a flange seven inches in diameter and is provided with a cast-iron cover one inch in thickness, which can be firmly fastened to the flange by means of six one-half inch bolts.

In charging the crucible, sodium chloride, finely ground and thoroughly dried, was first put in to the depth of about an inch and a half, and this was then well pounded down with a wooden plunger to compact the salt and expel the enclosed air. On top of the salt were placed alternate layers of potassium fluozirconate, also thoroughly dried, and metallic sodium, these being pounded down as before. The remaining space in the crucible was then filled with sodium chloride and, after pounding this down, the top was bolted on and the crucible was heated for about three hours with three triple burners. This heat, however, was not sufficient to raise the crucible to redness.

The crucible was then allowed to cool and, upon opening it, the charge was found to be so compact that it had to be loosened with a chisel. On treating the mass with water the metallic zirconium, together with a small amount of the oxide which had formed, settled to the bottom while the sodium chloride and potassium and sodium fluorides dissolved.

The zirconium and zirconium oxide were separated by first floating off the lighter zirconium with water and then digesting it with dilute hydrochloric acid at 40° until all of the oxide had been dissolved. The resulting product was a black, amorphous powder which, after washing with water, alcohol, and then with ether, showed no trace of impurity before the spectroscope except a slight amount of sodium.

Vapor of iodine was passed over some of this zirconium heated to dull redness in a current of hydrogen, but with no better success than with the other sample. We then concluded to substitute hydriodic acid gas for the iodine. Considerable difficulty was encountered in finding a suitable method of preparing the gaseous hydriodic acid. That described by Merz and Holzmann[1] was finally found to answer admirably. It consists in passing dry hydrogen and vapor of iodine through a red hot tube filled

[1] *Ber. d. chem. Ges.*, **22**, 867.

with pumice stone and freeing the hydriodic acid gas from iodine by passing the gases through cotton.

In treating the zirconium with hydriodic acid gas the following apparatus was used.

Iodine was placed in a small tubulated flask connected on one side with an apparatus furnishing pure, dry hydrogen and on the other side with a long piece of combustion tubing. The half of this tube nearest the iodine flask was filled with pieces of pumice stone and rested in a combustion furnace. The other half, extending beyond the combustion furnace, was filled with cotton. The end of this tube was connected with another combustion tube resting in a second combustion furnace. The porcelain boat containing the zirconium was placed in this second tube.

The hydrogen was first passed through the whole apparatus for several hours and then the first furnace was lighted. When the pumice had become red hot the flask containing the iodine was gently heated. The tube containing the zirconium soon became filled with the hydriodic acid gas, whereupon the second furnace was lighted. As the temperature rose, a brownish-yellow substance collected in the cold end of the combustion tube, but as the heat became greater the color entirely disappeared and there remained an amorphous white sublimate. No further sublimate was formed until the tube had almost reached a bright red heat when there appeared just beyond the point where the tube was red hot a white crystalline sublimate, different in appearance from that which first formed. The gas escaping from the end of the tube contained hydriodic acid, hydrogen, some iodine, and a trace of iron, the last probably being present in traces in the zirconium and volatilizing as ferrous iodide. The tube was kept at a bright red heat for from three to four hours. The gas was then turned off and when the boat had cooled considerably the heating of the iodine flask was discontinued. The first furnace was then shut off and the whole apparatus was allowed to cool in the current of hydrogen.

The material in the boat had changed from a black to a grayish-white color, but a chemical examination showed that it contained very little iodine. The amorphous sublimate which first

formed was found not to be zirconium iodide but to contain chiefly iron and iodine.

The crystalline sublimate which was formed only at a red heat was next analyzed. These crystals were found to be insoluble in water, nitric acid, hydrochloric acid, aqua regia, and carbon disulphide. They were decomposed and dissolved by concentrated sulphuric acid; they were also decomposed, but not completely, by concentrated nitric acid, iodine being liberated and a white powder, insoluble in the nitric acid, remaining. This residue was soluble in concentrated sulphuric acid and from this solution ammonium hydroxide threw down a white gelatinous precipitate. Upon dissolving this precipitate in hydrochloric acid and dipping turmeric paper into the solution, the orange color characteristic of zirconium was obtained. The solution gave no reaction for iron.

The zirconium in the compound was quantitatively determined by expelling the iodine by heating a portion of the salt with a mixture of sulphuric, nitric, and nitrous acids, dissolving the residue in concentrated sulphuric acid, diluting with water, and precipitating the zirconium with ammonium hydroxide. The precipitate was washed, dried, and ignited, and the zirconium weighed as the dioxide.

The iodine was determined by fusing some of the compound with about five times its weight of a mixture of potassium and sodium carbonate. The mass was then treated with water, filtered, and after acidifying the filtrate with nitric acid the hydriodic acid was precipitated with silver nitrate and weighed as silver iodide.

The results were

	Calculated for ZrI_4.		Found.	
	Per cent.	Per cent.	Per cent.	Per cent.
Zirconium	15.15	15.17	15.00	15.37
Iodine	84.85	85.34	85.27	....

The crystals when examined under the microscope proved to be clear, colorless cubes which showed no double refraction.

When heated for some hours in hydrogen the zirconium tetraiodide becomes black and iodine and hydriodic acid are formed. Heated in the air the iodide melts and sublimes. A weighed amount was placed in a porcelain crucible, covered with water,

and evaporated to dryness. No change in weight and scarcely any in color resulted after two such treatments. This behavior toward water is surprising, for from the published descriptions of zirconium tetrachloride and tetrabromide, it was to be expected that the iodide would prove to be a hygroscopic compound easily decomposed by water. It seems, however, to more nearly resemble the fluoride which Deville states to be a colorless crystalline substance volatile at a white heat and insoluble in water or acids.

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PHTHALIMID.[1]

BY J. A. MATHEWS.

Received June 9, 1896.

A NUMBER of years ago Prof. C. E. Colby and Mr. Dodge, of Columbia University were led to try the effect produced by heating together, under pressure, mixtures of (1) fatty acids and fatty nitrils; (2) fatty acids and aromatic nitrils; (3) fatty nitrils and aromatic acids; and (4) aromatic acids and aromatic nitrils. The reactions were carried on in sealed tubes. The score or more reactions that they tried were done at temperatures ranging from 235° to 280° C. As the result of their work they reached these conclusions regarding what is likely to take place, at least when monobasic acids and mononitrils are employed.[2]

1. Fatty nitrils and fatty acids give secondary amids.

2. Fatty nitrils and aromatic acids give fatty acids and aromatic nitrils.

3. Aromatic nitrils and fatty acids give mixed secondary amids.

4. Aromatic nitrils and aromatic acids gave secondary amids, except in one case when exceptionally high heat was used (280°) in which case the cyanide of the higher radicle was formed.

In regard to dibasic acids and dicyanides not so much has been done. Miller first tried reactions with succinic acid and ethylene cyanide.[3] He found that succinimid resulted from each of the following experiments:

[1] Read before the American Chemical Society. New York Section, June, 1896.
[2] *Am. Chem. J.*, 13, *1891*.
[3] This Journal, 16, 443, *1894*.

1. Ethylene cyanide and acetic acid heated in a sealed tube.
2. Acetonitril and succinic acid, and
3. Ethylene cyanide and succinic acid.

Some other acids in this series have been tried. Malonic acid was rather imperfectly tested. In every case the tubes exploded and malonimide was not obtained at all.

Seldner[1] reports parallel results to those obtained by Miller when he used glutaric acid and trimethylene cyanide. In the following trials which he made glutarimid resulted every time:

1. Glutaric acid (1 mol.) and acetonitril (2 mols.).
2. Glutaric nitril (1 mol.) and acetic acid (2 mols.).
3. Glutaric acid and glutaric nitril, equal molecules.

Until the writer, at Prof. Colby's suggestion, made the experiments hereinafter recorded no one, to my knowledge, had applied these methods to aromatic, dibasic acids. The results of the first experiments are very gratifying and I hope in the near future to try the reaction with other dibasic, aromatic acids.

Since no information regarding phthalic nitril could be obtained I was obliged to do without it. The experiments were therefore made with phthalic acid and propionitril.

Four sealed glass tubes each containing phthalic acid (1 mol.) and propionitril (2 mols.), plus about three drops of acetic anhydride were heated in an oven for various lengths of time and at different temperatures.

Tube I. The first tube was opened after ten hours heating at 180° C. The contents of the tube had a pungent acid odor and were treated with cold dilute potassium carbonate solution. A residue consisting of needle-like crystals remained. These were filtered off, washed with water, and dried. The crystals then had a melting point of 228° C. I immediately suspected from this melting point that phthalimid had been formed by the reaction

$$C_6H_4(COOH)_2 + C_2H_5CN = C_6H_4(CO)_2NH + C_2H_5COOH.$$

The yield of phthalimid in this experiment was about sixty per cent. of the theoretical.

[1] *Am. Chem. J.*, 17, 1895.

Tube II. On heating the remaining three tubes higher No. 2 broke at about 215°.

Tube III. After further heating of eight hours at 200° to 215° C. the third tube was opened and the contents treated with potassium carbonate solution. The crystals remaining were not so light colored as those from Tube I, and were so different in appearance that it was thought some other reaction had taken place. The melting-point, however, was about the same as in the first case, *viz.*, 227°. Yield eighty-four per cent.

Tube IV. Exploded at 258° C.

Since the theoretical equation requires only one molecule of nitril to one of phthalic acid two more tubes were prepared, each containing equal molecules of phthalic acid and propionitril.

Tube V. After three and a half hours at 180°–200° C. the fifth tube was opened and treated with potassium carbonate solution as before. Residue crystalline; melting-point 228.5°, yield eighty-eight per cent.

Tube VI. Heated five and a half hours at 180°–200°, melting point of residue, insoluble in cold, dilute potassium carbonate solution, 228.3° C., yield 92.5 per cent.

The crystals of phthalimid were all more or less colored, the color being darkest in the case of the third tube which had been subjected to long, high heat. In no instance was any outward pressure noticed on opening the tubes.

Portions of the products were recrystallized from acetic acid, from alcohol, and from alcohol with the addition of animal charcoal to decolorize. The melting points of the recrystallized products were a little higher than before purification, *viz.*, 230°, 229.5° and 229.5°, respectively. These agree very closely with the point given in Beilstein.

Biedermann[1] gives the melting-point as 228° or 229° C.

Michael[2] gives the corrected melting-point as 233.5° C. The decolorized crystals from alcohol form beautiful long needles.

Notwithstanding the close agreement of the melting-points obtained with those given by the authorities, some other tests were made to show that the product was nothing else than

1 *Ber. d. chem. Ges.*, 10, 1166.

2 *Ber. d. chem. Ges.*, 10, 579.

phthalimid. A portion of the crystals heated with potassium hydroxide went into solution with evolution of ammonia. Another portion of the crystals were covered with concentrated ammonia and allowed to stand for some time. They were soon converted into microscopic crystals of phthalamid

$$(=C_6H_4(CONH_2)_2).$$

These crystals were filtered off, washed, and dried. They melted at 217.5° (uncorrected) with an evolution of ammonia, which began at about 200°. The phthalamid was further proved by its insolubility in cold water, alcohol, and ether, and by boiling it with water it was decomposed, giving off ammonia and on cooling phthalimid, melting at 230° C., crystallized out.

The results of these tests show conclusively that the product is phthalimid and that when it is made by the action of equal molecules of acid and nitril the yield is large. The reaction works comparatively readily, and at a much lower temperature than was needed to affect the reactions recorded by Colby and Dodge. It is highly probable that with slight changes of conditions any one of a variety of nitrils would give the same result. I hope to report further experiments with phthalic acid and other dibasic aromatic acids at a later day.

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DETERMINATION OF SULPHURIC ACID.

BY N. J. LANE.

Received May 19, 1896.

SOME months ago, before hearing of the controversy between Dr. Lunge and Mr. Gladding, some experiments were made on this subject, the results of which sustain Mr. Gladding's case. The determinations were made on nearly normal sulphuric acid to establish its strength with the following results:

	Barium chloride added suddenly.	Barium chloride added by drops.
1. Sulphuric acid	50.03	49.23
2. " "	49.90	49.32
3. " "	50.14	....

And the average of several practically identical titrations on C. P. sodium carbonate gave sulphuric acid 49.33.

The above results were obtained with the greatest care, and every precaution used to insure accuracy. This, in my opinion, conclusively proves the accuracy of Mr. Gladding's statements.

NOTE ON THE SOLUBILITY OF BISMUTH SULPHIDE IN SODIUM SULPHIDE, WITH SPECIAL REFERENCE TO THE ESTIMATION OF SMALL AMOUNTS OF BISMUTH IN ANTI-FRICTION ALLOYS.

By Thomas B. Stillman.

Received June 16, 1896.

THE method of separation of lead, copper and bismuth from antimony, arsenic and tin by the use of sodium sulphide is quite general. This is dependent upon the usually accepted statement that the sulphides of bismuth, lead and copper are insoluble, and the sulphides of arsenic, antimony and tin are soluble in sodium sulphide. This process of separation is employed in the analysis of various alloys, especially of anti-friction alloys, containing lead, tin, antimony, etc.

An alloy, used for similar purposes, but containing, in addition to lead, copper, antimony and tin, a very small amount of bismuth, was recently submitted to me for analysis.

After complete solution of the alloy in hydrochloric acid with a few drops of nitric acid, the acid was neutralized with sodium hydroxide, sodium sulphide solution (1.06 sp. gr.) added and the heat applied for twenty minutes. The solution was filtered and the filtrate examined for the antimony and tin with satisfactory results.

The precipitate of insoluble sulphides remaining upon the filter was found to contain lead and copper, but no bismuth. This indicated that the small amount of bismuth which was present in the alloy had gone into solution in the sodium sulphide.

To prove this theory, I weighed 0.128 gram of pure bismuth nitrate, dissolved it in twenty-five cc. of water with a few drops of nitric acid, the clear solution neutralized with sodium hydroxide, seventy-five cc. solution of sodium sulphide added, and warmed to a temperature near boiling for twenty minutes. The solution was filtered from the bismuth sulphide, remaining insoluble in the sodium sulphide. The clear filtrate was rendered faintly acid with hydrochloric acid, when a brownish-black precipitate immediately formed. This precipitate was filtered, dissolved in

hot nitric acid and evaporated to dryness and ignited in a weighed porcelain crucible. The residue obtained was 0.031 gram of bismuth trioxide, and strongly yellow in color. It was dissolved in a few drops of hydrochloric acid, and the three following confirmatory tests for bismuth were made:

1. A portion of the solution was poured into a large amount of water, forming immediately a white precipitate of bismuth oxychloride.

2. A portion was tested by Schneider's test, the most delicate test for bismuth, the reaction obtained being strong and characteristic.

3. A portion was diluted with water, not enough to cause precipitation, and the solution saturated with hydrogen sulphide. The precipitate formed was brownish-black in color.

These three tests are absolutely confirmative of the presence of bismuth, and also show the absence of the other metals. By thus using pure bismuth nitrate for this test, lead, copper, antimony and tin are not present.

If now an analyst should weigh twelve grams of an alloy, composed approximately of lead eighty per cent., antimony fifteen per cent., tin 4.75 per cent., and bismuth 0.25 per cent. ("magnolia metal,") and sodium sulphide solution be used for the separation of the tin and antimony from the lead and bismuth, *all* of the bismuth present would pass into solution and escape determination by the analyst.

No analyst, however, would use as much as twelve grams of such an alloy for analysis, but rather one or two grams.

If one gram be taken and sodium sulphide used as above indicated, three per cent. of bismuth might be present and *all* of it pass into solution in the sodium sulphide instead of remaining as an insoluble sulphide with the lead sulphide.

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ON THE ESTIMATION OF SULPHUR IN PYRITES.

By G. Lunge.

Received June 19, 1896.

IT has taken Mr. T. S. Gladding six months to reply to my last paper on the above subject. I will not take much more than six days from the date of receiving the May number of the Journal of before dispatching my final reply to that gentleman.

Mr. Gladding avoids any mention, and of course offers no refutation, of the charges I had brought against him, but he again puts me into a totally false light, by saying that I "attempt no further support of my position by chemical experiment." This suppresses the fact that I had referred to my more than sufficient experimental proof for Mr. Gladding's and his assistants' inability to handle my process, which has been in daily successful use by scores, if not hundreds, of chemists for a number of years past, and is that employed in Fresenius' own laboratory, as I hear from his son-in-law and laboratory chief, Dr. Hintz. Mr. Gladding now exacts a further reply from me, more especially on the strength of some new comparative tests of what he states to be the main point at issue, namely the necessity of a very slow addition of the barium chloride.

I am convinced that our readers are as tired of this dispute as I am, but as some of them might construe my silence into the admission that Mr. Gladding is right on this point, and might saddle themselves with a total unnecessary complication in their daily work, I will not shirk a further reply, although I think it unnecessary after having quoted already in March, 1895, eleven experiments by entirely independent chemists, refuting all Mr. Gladding's assertions.

In his former paper Mr. Gladding states that the error caused by the rapid addition of the barium chloride solution is from two-tenths to three-tenths per cent. of sulphur, and according to his last paper it is even one-half per cent. He appeals to independent chemists to settle this discrepancy between his statements and my own. I have taken this up in the following manner: I instructed one of my assistants, Mr. U. Wegeli, a skilled

worker, but entirely ignorant of the above dispute, to make a series of very careful tests of a sample of pyrites, just arrived for analysis and belonging to an important commercial case. I enjoined him to give me absolutely unvarnished results (which in our laboratory it would not have been at all necessary to say), and I told him, as we must be quite sure of the matter, he must not merely employ all the ordinary precautions, but also try both the usual quick addition of the barium chloride and a process recently very much recommended, namely, the very slow addition of the precipitant; I did not express any opinion of my own upon that point, and left it entirely for him to find out what there was in the matter. I had just then to undertake a short journey, and on my return he handed to me the following results.

A. *Quick* addition (*i. e.*, pouring in the hot barium chloride solution in about ten portions, occupying about half a minute in all, and stirring the mixture all the time, as every chemist would do).

1. 39.83 2. 39.65 3. 39.65 per cent. sulphur.

B. *Slow* addition from a burette, one drop per second (exactly as described by Mr. Gladding).

4. 39.63 5. 39.69 6. 39.44 per cent.

This means: In No. 2 and 3 the quick addition has given *identical* results with the slow addition in No. 4 and 5. No. 1 shows a little more, No. 6 a little less. I have suppressed nothing, and I give these results as well, although they are evidently not as reliable as the other four, entirely concordant, results; but even if we admit the less reliable results in striking an average, we find a difference of only one-tenth per cent. between the quick (39.71) and the slow (39.59) process. Such a difference is evidently within the limits of ordinary experimental error.

ZURICH.

[This discussion closes with the present paper.—ED.]

BACTERIA IN MILK SUGAR.

By Albert R. Leeds.

Received June 6, 1896.

CERTAIN phases of bacteriological investigations command universal and profound popular interest, and any publication relating to the connection of a specific organism with a zymotic disease, elicits general attention and discussion. This intimate connection of bacteriology with questions of life and death, has led many to regard the study as the proper province of medical specialists, despite the first uses made of bacteriological methods by Pasteur and his followers and to neglect them as instruments of chemical research. But the morphology, the classification, the physiology, and the botany of the bacteria are in such a rudimentary and unsatisfactory condition that the most valuable methods of bacteriological investigation are still of a chemical nature. The preparation of the culture fluids, the application of the tests, and the isolation of the products are chemical operations, and the advances to be made in the near future are to be looked for mainly on the chemical side of the subject. For this reason the absence from the columns of this Journal of papers resting upon the bacteriological questions, has been a matter of surprise to the writer, and the important contributions which have been herein recently made by Dr. Schweinitz, Dorsett, Bennett, Pammel, and Mason, a source of congratulation. Their results foretell the rich harvest of the future when the complete quantitative value of the chemical actions involved are known, and the different views which they may be expected to inaugurate as to the nature of many bodies now grouped closely together, but which deport themselves very differently when bacteria are the reagents made use of.

It is for these reasons that the writer desires to put on record the slight observations which he has made during the course of ordinary chemical work. They spring out of some anomalous behavior of specimens of milk sugar, which were being examined for purity. All the samples of pulverized milk sugar coming from the drug stores, which he examined, proved to contain a ferment when their solutions were kept at the optimum tempera-

ture for a sufficient length of time. The lactic acid produced was isolated in the form of calcium lactate. This was not the case with some lactose crystallized in nodular masses of prismatic crystals which had been obtained originally from Kahlbaum, and had been standing for twenty-five years in a stoppered jar. It was sterile. With the exception of this specimen, all the others gave an abundant crop of bacteria when definite weights dissolved in sterilized water were submitted to ordinary gelatin-peptone culture. The maximum number obtained in this medium was 1400 colonies per gram of milk sugar. In studying these colonies I looked more particularly for the bacillus *acidi lactici* and the other ten or twelve species, which are at the present time classified as the specific milk bacteria, but without success. With a lactose-litmus gelatin solution a still larger number of colonies was obtained and possibly larger search in this medium, might have revealed the specific milk bacteria of lactic acid fermentation. But my immediate object had been attained, and the presence of bacteria as a common impurity in lactose, to be looked for and avoided by the chemist and the druggist, sufficiently demonstrated.

THE QUANTITATIVE DETERMINATION OF THE THREE HALOGENS, CHLORINE, BROMINE AND IODINE, IN MIXTURES OF THEIR BINARY COMPOUNDS.

BY A. A. BENNETT AND L. A. PLACEWAY.

Received June 2, 1896.

CHEMICAL literature contains many records of methods for the quantitative estimation of the halogen elements, and for any one of these elements in the absence of the others they are as satisfactory as may be required. There are also, it is true, many suggestions and several proposed methods for the separation and estimation of these elements when present together or when some two are found in the same mixture, although they are generally unsatisfactory for one reason or another. The methods for qualitative determinations as given by Hart and by Kebler, in the *Journal of Analytical Chemistry*, are thoroughly satisfactory. A very convenient qualitative method that is in use

in this laboratory consists in first using chlorine water, or euchlor, (made from potassium chlorate and hydrochloric acid), which immediately determines the presence or absence of iodine and in its absence that of bromine. Carbon bisulphide is used as the final indicator. If iodine is present more chlorine water is added and the whole is heated until the iodine color is replaced by the light yellow color due to bromine. This point is easily discerned. If now one or more of these halogens are present a portion of the original solution is treated with concentrated nitric acid and boiled until both of these elements are removed. This solution is now tested for chlorine by the usual methods.

There are several methods for the quantitative estimation of the halogens by the formation of their silver salts, the further treatment depending on whether two or three of these elements are present. In all cases, however, much time is required for the analysis and great care in the manipulation of the precipitates. Sexton says, in his work on Quantitative Analysis, Third Edition, that there is no known method by which the two acids, hydrogen bromide and hydrogen chlorine can be completely separated. He recommends their precipitation as silver salts, the weighing of this product and the conversion of the bromide present into the chloride by passing chlorine gas over the fused mixtures. From the results the amount of each halogen is determined. Of course the general procedure could be used if an iodide were associated with the chloride but would not be applicable in case all three halogens were present.

Dr. Prescott, in the *Journal of Analytical Chemistry*, **3**, gives an acceptable method for the estimation of bromine in the presence of chlorine and calls attention to several others that have been employed. Fresenius gives, on pages 592 to 600 in the Second American edition of his work on Qualitative Analysis, elaborate methods for determining these elements in all possible mixtures of the binary compounds of these elements. They are generally difficult of application and employ rare reagents. It may be said, in general, that all methods of indirect estimation of the halogens in mixtures of their binary compounds are troublesome, although some of the recent modifications of these

methods give fairly satisfactory results, especially in the separation of two of the elements like chlorine from bromine.

The authors, therefore, began the examinations of several of the recent methods for the direct estimations of these elements. The method of M. Dechan was tested and found to produce too low results for the chlorine since a portion of it was set free as hydrogen chloride by the action of the sulphuric acid added after the iodin was supposed to be set free. In the original contribution[1] the author directs that the volume of the liquid in the distilling flask must not be much reduced and never below two-thirds of the original amount. Even then the amount of the chlorine is low. Under the conditions required by M. Dechan the bromine is satisfactorily separated from the chlorine and the iodine from both.

In 1885, Dr. Hart published a method for the qualitative determination of these three elements in mixtures of their binary compounds. This method suggested the method developed by the authors for the quantitative estimation of these elements.

The alkali salts of these three elements were purified and dissolved in separate solutions. The salts were taken to be pure at the start and accordingly ten grams of each of the salts was dissolved each in a liter of water. The mixtures were made from these solutions by carefully measuring definite volumes and thoroughly mixing. In this way solutions containing varying amounts of any one of the salts were prepared. The salts were afterwards found to be somewhat impure and the proper correction for this impurity has been made in the tables.

Ferric ammonium alum was used to free the iodine. The solution was made from the crystallized alum, using 200 grams to the liter. The potassium permanganate solution was a saturated solution. This was used in a concentrated form, since considerable was required to oxidize the iron that had been reduced by the iodine. The solution for the absorption of the iodine and bromine contained 200 grams of potassium iodide to the liter and thirty-five cc. were used in the receiver.

The apparatus finally found to be the best for the distillation consisted of a 500 cc. Wurtz flask with the side tube inserted

[1] *J. Chem. Soc.*, 49.

quite near the bulb of the flask. The condenser was made with a long inner tube so that it could be bent at the lower end at the proper angle to fit into the receiver. A rubber stopper was slipped on the bent end so that when the tube was inserted in the receiver it would reach into the absorbing liquid. The best receiver was a three-bulbed U tube of about 250 cc. capacity. The upper end of the distilling tube was slightly smaller than the somewhat enlarged mouth of the inner tube of the receiver so that although the former did not enter the tube yet when they were brought together and covered by a piece of rubber tubing the latter was protected from any iodine or bromine vapors. The limb of the U tube into which the bent tube of the condenser passed was stopped by a rubber stopper. In a number of the estimations a second absorption tube was attached to the usually open limb of the U tube but in no case did any recognizable amount of iodine or bromine vapor escape.

The distillations were carried on as follows: To the distilling flask was added fifty cc. of the iron sulphate solution and to this water enough to make about 200 cc. The halogen salt solutions were carefully measured from burettes into the flasks. The proper connections were made and the distillation carried on for twenty-five minutes after the liquid had reached boiling temperature. Some fifteen or twenty glass beads were added to prevent bumping. The flasks were heated by a flat four and one-half inch burner. The flask and burner were carefully protected from currents of air to prevent the drawing back of the liquid in the receiver. It was found that the rubber stopper in the distilling flask of the form indicated was not noticeably attacked by the vapors in course of about 100 determinations.

When the distillation had been completed, as just described, the flask was detached from the condenser, the tube of which was washed with a warm solution of potassium iodide followed by hot water. Another receiver prepared exactly as for the absorption of the iodine was now attached to the condenser. Thirty-five cc. of potassium permanganate solution was now added, and with it water in sufficient quantity to make the volume about 200 cc., the connections made and the distillation carried on until the bromine was all set free. Twenty-five min-

utes time was used for each distillation, but less time was usually sufficient. In fact most of the halogens were driven over during the first few minutes of heating after boiling temperature was reached. In case very great accuracy is not required an estimation can be completed in a few minutes.

It is evident that in all cases there must be relatively large excess of reagents. When the distillations were complete the iodine set free in the receiver was titrated against decinormal sodium thiosulphate. The titration can be made in the receiver but it was found most convenient to pour the liquid into a six-inch evaporating dish before estimation.

The contents of the flask are now removed to a beaker and the excess of the permanganate reduced by ferrous sulphate, adding sulphuric acid enough to render the solution clear. The solution was slightly warmed to hasten the action. It was then cooled and made up to a definite volume and an aliquot part estimated by precipitation with silver nitrate. There was nothing to prevent the estimation of the chlorine by titration, but no determinations were made by that method.

The following tables give the results of the work:

	Potassium iodide taken.	Iodine in potassium iodide.	Iodine found.	Potassium bromide taken.	Bromine in potassium bromide.	Bromine found.	Potassium chloride taken.	Chlorine in potassium chloride.	Chlorine found.
1	0.986	0.0754	0.0745	0.198	0.1330	0.1329	0.994	0.4869	0.4829
2	0.493	0.0377	0.0374	0.198	0.1330	0.1299	0.994	0.4869	0.4859
3	0.493	0.0377	0.0377	0.099	0.0665	0.0658	1.988	0.9738	0.9699
4	0.493	0.0377	0.0376	0.099	0.0665	0.0662	0.994	0.4869	0.4870
5	0.493	0.0377	0.0378	0.099	0.0665	0.0659	0.994	0.4869	0.4858
6	0.493	0.0377	0.0375	0.0495	0.0332	0.0328	0.994	0.4869	0.4867
7	0.493	0.0377	0.0375	0.0495	0.0332	0.0331	0.994	0.4869	0.4857
8	1.972	0.1508	0.1499	0.099	0.0665	0.0664	1.988	0.9738	0.9679
9	1.972	0.1508	0.1484	0.099	0.0665	0.0659	0.497	0.243	0.241
10	0.493	0.0377	0.0375	0.0495	0.0332	0.0329	0.497	0.243	0.242

The tabular statement needs no particular explanation. The quantities represented are the amounts in grams in each case.

It may be well to note that this general method is applicable for rapid technical estimations of bromine or of iodine either by themselves or in case of mixtures of the same. Single analyses can be readily made in ten to fifteen minutes.

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ON THE INVERSION OF SUGAR BY SALTS. NO. 2.

By J. H. Long.

Received June 29, 1896.

In a recent paper[1] I have shown that in their behavior with cane sugar solutions many so-called neutral salts closely resemble weak mineral acids. Salts of the heavy metals in general have the power of inverting sugar solutions, and in some cases very rapidly, especially at an elevated temperature. The same fact has been pointed out for certain salts by others, notably by Walker and Aston,[2] who determined the speed of inversion of four nitrates, comparing them with dilute nitric acid. This inversion is due to the hydrolysis of the salts in question, the hydrogen of the acids formed being in all cases, probably, the active catalytic agent.

In my former paper I gave some results obtained in a preliminary investigation on ferrous iodide with very strong sugar solutions, and in the present paper I shall give the results obtained with other salts, as well as more extended tests with the iodide.

METHOD.

In the experiments before reported I made very strong syrups containing usually fifty grams of sugar in 100 cc., and to these syrups before final dilution weighed amounts of the salts were added, the volume being brought up to 100 cc. with distilled water. In the following series of tests the amount of sugar present is much smaller, being in all cases fifty grams in 250 cc. of the finished solution. This solution is much stronger than is usually employed in inversion experiments, but with many of the salts dissolved weaker sugar solutions could not be well used. The ferrous salts, especially, require relatively large amounts of sugar to hold them in clear solution, and as many of the experiments given below were made on such salts, it was decided to employ the same weight of sugar in all cases. For each experiment, therefore, fifty grams of pure sugar was dissolved in water in a 250 cc. flask by aid of heat. The strong syrup was cooled and to it was added the salt in the powdered form or dissolved in a little water. After securing a complete

[1] This Journal, 18, 120.

[2] *J. Chem. Soc.*, July, 1895.

solution in either way, it was diluted to the mark and shaken to mix thoroughly.

The syrup so made was poured into small tubes of thin glass for inversion. These tubes held about twenty cc. and were three-fourths filled. They were cleaned for use by boiling in hydrochloric acid and then in distilled water repeatedly. After having been employed for several series of tests it was found sufficient to soak them twenty-four hours in weak acid, and then in distilled water, rinsing thoroughly finally. After receiving the sugar solutions they were closed with perforated rubber stoppers holding each a short glass tube with capillary opening. The tubes were placed in a receptacle, which was finally immersed in the water of a thermostat holding over twenty liters. The receptacle for the tubes consists essentially of two copper disks, twenty-five cm. in diameter, soldered six cm. apart on a copper rod as an axis. The lower disk is furnished with fine perforations, and the upper one with larger openings to receive the tubes. The copper axis below the lower disk ends in a hardened point, resting in a socket, and is extended above to a length of fifteen cm., ending in a grooved pulley around which a belt passes. Power applied to this belt rotates the tube receptacle, which at the same time keeps the water of the thermostat in motion. The thermostat itself consists of a large copper oven covered with asbestos boards on five sides. The top has perforations for the temperature regulator, thermometer and rotating axis of the tube receptacle. A section of the top can be quickly removed to take out tubes, but at other times should be left closed to exclude light. The capillary tubes in the stoppers closing the inversion tubes project about two cm. above the water.

With the apparatus employed it was possible to maintain a constant high temperature with a little watching through ten hours. A temperature of 85° was held with variation of less than 0.1° in either direction. With many salts the rate of inversion is exceedingly slow at ordinary temperatures, in fact almost imperceptible. For convenience in working, therefore, it was found necessary to invert at a high temperature, and 85° was

chosen. In a few instances a slightly higher temperature was employed, but the results obtained are not included below.

The reaction between the sugar and salt is probably in most instances analogous to that between sugar and weak acids, and the rate of inversion may therefore be expressed by the same differential equation:

$$\frac{dx}{dt} = K(A - x).$$

The integration of this for t and $x = 0$, together, leads to the well known formula:

$$K = \frac{1}{t} \text{ nat. log. } \frac{A}{A - x},$$

where A represents the amount of sugar present at the beginning of the inversion, x that inverted at any time, t, of an observation, and K the "constant" or "coefficient" of inversion.

As the reaction is most easily followed by means of the polaristrobometer, A is conveniently measured by the total change in rotation which is observed between the beginning of the reaction and after complete inversion. x is measured by the change of rotation from the beginning up to the time, t, of any observation. For convenience common logarithms are employed in all the calculations below. As the sugar solutions were mixed with the inverting substances at a low temperature, the intervals, t, could be reckoned only from the time when the mixtures in the tubes had reached the constant temperature of the experiment. Preliminary tests were therefore made to determine several points of practical manipulation. The thermostat was first brought to a temperature of about 87°–88°, and the filled experimental tubes and their receptacle immersed in it. From this a fall of temperature resulted, because of the low temperature of the solution. In five or six minutes the constant temperature of 85° was reached, and by regulation of the gas flame this was maintained. In another set of experiments it was found that the solutions in the experimental tubes could be brought to a temperature of 85° from the room temperature in four to six minutes. It appeared, therefore, that ten minutes was amply sufficient time to allow, after introducing the tubes into the

thermostat, before beginning the actual observations, and this was done in all cases in the experiments given below. In the case of bodies which invert but slowly there is little objection to the loss of this first ten minutes of the reaction, but in a few instances it was found to be a decided drawback, as will be seen below.

Usually 250 cc. of the solution was prepared for experiment, and this was filled into fifteen or sixteen tubes, and put into the thermostat. At the end of ten minutes a tube was withdrawn and cooled very quickly by immersion in cold water, or by holding it under a flowing hydrant. The contents were then poured into a polarization tube and polarized at the constant temperature of 20° in most cases. In a few tests made in warm weather a temperature of 25° was maintained in the dark room and in the water flowing around the observation tube. This first observation gives the initial rotation, and the time of removing the tube may be put as $t = 0$. Tubes were removed at different intervals following and treated in the same manner. The results of the polarizations were always very constant during the first few hours heating in the thermostat, as was found by removing and polarizing the contents of three tubes, but after five or six hours less regular results were found, and I adopted the plan of taking the mean result obtained by examining two or three tubes. With fifteen or sixteen tubes I made observations at eight or nine intervals.

After polarizing the liquids in the last tubes removed, the contents were mixed, returned to a tube and heated longer to obtain the end point of the reaction, that is, the point of complete inversion. The point found in this manner does not always agree with that calculated from the known weight of pure cane sugar in the original solution. Even with dilute acids the phenomenon of inversion is not as simple a thing as usually represented. As shown by Gubbe[1] and others, the specific rotation of invert sugar depends not only on the concentration, but on the time, temperature and acid used. Prolonged heating with salts produces in many cases, apparently, a slight

[1] *Ber. d. chem. Ges.*, 18, 2207.

decomposition of the levulose, from which the negative rotation of the invert sugar is found smaller than it should be theoretically. In a few instances, however, the negative rotation of the invert sugar was increased. From the experiments of Gubbe it may be calculated that fifty grams of cane sugar in 250 cc. would yield a solution after inversion, which in a 200 mm. tube should show a negative rotation of $-8.6°$. The rotation observed in my experiments was usually about $-8.3°$, but an accurate determination was not always possible, as some of the solutions became slightly colored before inversion was quite complete, and in other cases a negative rotation once observed seemed to grow slightly less on longer heating, making the exact end point somewhat uncertain. The discrepancies were not large in any case, however, and I decided to take $-8.3°$ as the true end point for the 200 mm. tube, and $-4.15°$ for the 100 mm. tube.

With some of the salts examined the velocity coefficient, K, is practically constant, with others it increases with the time, while in still other cases it decreases.

The sugar used in all the experiments was crystallized cut loaf of high degree of purity, and selected for the purpose. With fifty grams in 100 cc. it yields a solution of almost perfect clearness, which can be easily polarized in a 400 mm. tube. Weaker solutions yield, on inversion, results which agree perfectly with the theoretical requirement.

POTASSIUM ALUM.

Solutions of this salt invert very rapidly. A sample of pure alum was crystallized several times from distilled water to secure a product free from traces of uncombined sulphuric acid, sometimes present in the commercial article. This carefully purified salt was used in all the inversion tests. In the tables below, t refers to the time in minutes, and under α is given the observed angle of rotation in degrees and hundredths.

Experiment 1.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{64}$.

In 250 cc., fifty grams of sugar + 0.617 gram of alum.

$$A = 33.03°.$$

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	24.73°	....	....	....
15	20.15	4.58°	0.06483	0.00432
30	16.16	8.57	0.13045	0.00434
60	9.75	14.98	0.26243	0.00437
90	4.85	19.88	0.39998	0.00444
120	1.25	23.48	0.53891	0.00449
150	—1.30	26.03	0.67581	0.00449
210	—4.88	29.61	0.98488	0.00468
270	—6.40	31.13	1.24016	0.00459
				0.00446

Experiment 2.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{32}$.

In 250 cc., fifty grams of sugar + 1.234 grams of alum.

$$A = 32.37.$$

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	24.07°	....	....	....
15	17.83	6.24°	0.09300	0.00620
30	12.92	11.15	0.18339	0.00611
60	5.50	18.57	0.37026	0.00612
90	0.75	23.32	0.55349	0.00615
120	—2.48	26.55	0.74522	0.00621
150	—4.76	28.83	0.96114	0.00641
210	—7.00	31.07	1.39620	0.00661
270	—7.80	31.87	1.81117	0.00670
				0.00632

EXPERIMENT 3.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{16}$.

In 250 cc., fifty grams of sugar + 2.468 grams of alum.

$A = 31.25$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	22.95°	....	....	....
15	14.80	8.15°	0.13124	0.00875
30	8.79	14.16	0.26211	0.00873
60	1.07	21.88	0.52311	0.00872
90	—3.03	25.98	0.77304	0.00859
120	—5.64	28.59	1.06997	0.00891
180	—7.53	30.48	1.55533	0.00864
240	—8.15	31.10	2.31866	0.00966
				0.00886

EXPERIMENT 4.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{8}$.

In 250 cc., fifty grams of sugar + 4.936 grams of alum.

$A = 30.03$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	21.73°	....	....	....
15	11.23	10.50°	0.18686	0.01245
30	4.45	17.28	0.37205	0.01240
60	—2.87	24.60	0.74276	0.01238
90	—5.95	27.68	1.10649	0.01230
120	—7.34	29.07	1.49529	0.01244
180	—8.18	29.91	2.39838	0.01332
				0.01255

EXPERIMENT 5.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{4}$.

In 250 cc., fifty grams of sugar + 9.872 grams of alum.

$A = 29.19$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	20.89°	....	....	....
10	10.89	10.00°	0.18216	0.01822
25	2.10	18.79	0.44820	0.01793
50	—4.70	25.59	0.90893	0.01818
90	—7.73	28.62	1.70936	0.01899
150	—8.25	29.14	2.76626	0.01844
				0.01835

An attempt was made to invert with a half normal solution but at the temperature employed the rate was found to be too rapid for accurate observation.

With the first four solutions no difficulty was found in making accurate polarimetric observations in the 200 mm. tube. The last solution, however, became finally somewhat colored, and slightly turbid from precipitation of what appeared to be aluminum hydroxide. A portion, heated 180 minutes, became too turbid for direct reading and had to be examined in the 100 mm. tube after filtration. The rotation was found now to be —3.60°, corresponding to —7.20° for the 200 mm. tube, instead of —8.25° or —8.30°. From the slight concentration due to the filtration a still greater negative value instead of a lower one should be expected. We have here an illustration of the fact referred to above, *viz.*, that prolonged heating makes the end point determination somewhat uncertain at times.

It is interesting to note the relation existing between the concentrations of the solutions and their rates of inversion in the above examples. For comparison we can call the lowest concentration unity and arrange them as follows:

Conc.		K.
$\frac{N}{64}$	1	0.00446
$\frac{N}{32}$	2	0.00632
$\frac{N}{16}$	4	0.00886
$\frac{N}{8}$	8	0.01255
$\frac{N}{4}$	16	0.01835

Inspection of the table shows that the coefficient, K, increases rapidly with the concentration, but is not directly proportional to it. It is apparent that the numbers in the third column vary approximately as the square roots of those in the second, which is clearly shown in the next table.

Conc.	K.	$K_1 \times \sqrt{\text{Conc.}}$
1	0.00446	0.00446
2	0.00632	0.00631
4	0.00886	0.00892
8	0.01255	0.01261
16	0.01835	0.01784

The regular results obtained from the aluminum salt are probably due in a measure to the inertness of the hydroxide toward sugar, as well as to the behavior of sulphuric acid in inversion. The bases of the other salts examined below form combinations with sugar more or less readily, not only with saccharose, but also with the products of inversion, so that the normal results of the reaction may be modified in a manner difficult to compute. The rather rapid rate of inversion in the above points to a relatively great degree of hydrolysis in the alum. Walker and Aston[1] found something similar in a half normal solution of the nitrate, studied at a temperature of 80°. From their polarizations a value of 0.0077 for K was found, and this was much in excess of the values found for other salts at the same time.

FERROUS SULPHATE.

A sample of the purest obtainable sulphate was recrystallized from water containing a trace of sulphuric acid, then dissolved in distilled water and precipitated by alcohol. The crystal meal secured was washed several times with alcohol and dried by fanning. The finished product was bright green and gave a nearly clear solution with pure water. It still held a trace of alcohol as disclosed by the odor. The experimental solutions were made by dissolving the sugar first and adding to this syrup the weighed sulphate meal. The mixtures were shaken to complete solution without application of heat, and then poured into the tubes for inversion. The solutions soon became turbid on warming and a minute amount of flocculent precipitate separated, making direct polarization impossible. The readings could be made therefore only after filtration, which was not without slight effect on the result. The total amount of separated hydroxide or basic salt was and remained through the test, minute.

1 *Loc. cit.*

EXPERIMENT 6.

$FeSO_4.7H_2O$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 17.38 grams of sulphate.

$A = 17.12$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	12.97	....	......	......
15	12.48	0.49	0.01261	0.00084
45	11.50	1.47	0.03899	0.00086
75	10.40	2.57	0.07064	0.00094
135	8.43	4.54	0.13382	0.00099
195	6.72	6.25	0.19727	0.00101
255	5.21	7.76	0.26222	0.00102
375	2.87	10.10	0.38716	0.00103
495	1.03	11.94	0.51917	0.00105
				0.00099

EXPERIMENT 7.

$FeSO_4.7H_2O$. N.

In 250 cc., fifty grams of sugar + 34.75 grams of sulphate.

$A = 17.10$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	12.95	....	......	......
15	12.45	0.50	0.01289	0.00086
45	11.26	1.69	0.04520	0.00100
75	10.08	2.87	0.07980	0.00106
135	8.07	4.88	0.14593	0.00108
195	6.30	6.65	0.21388	0.00110
255	4.70	8.25	0.28606	0.00112
375	2.25	10.70	0.42682	0.00114
495	0.15	12.80	0.59953	0.00121
				0.00107

Other tests were made with a second preparation of ferrous sulphate from which the alcohol had not been as completely removed. For a half normal solution the coefficient, 0.00094, was found, and for a normal solution the value, 0.00100, both results being but a trifle lower than those obtained from the pure products. It is possible that the differences may be due to the presence of the trace of alcohol. In any case it is evi-

dent that with solutions as strong as those used the larger amount of sulphate inverts but little more rapidly than the smaller.

AMMONIUM FERROUS SUPHATE.

But one experiment was made with this salt, a very nice crystallized preparation being used.

EXPERIMENT 8.

$(NH_4)_2Fe(SO_4)_2.6H_2O.$ $\frac{N}{2}$.

In 500 cc., 100 grams of sugar + 49 grams of sulphate.

$A = 17.08.$

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	12.93	....	......	......
17	12.49	0.44	0.01134	0.00066
45	11.74	1.19	0.03137	0.00069
75	10.93	2.00	0.05409	0.00072
105	10.13	2.80	0.07776	0.00074
165	8.60	4.33	0.12698	0.00077
225	7.30	5.63	0.17368	0.00077
345	4.60	8.33	0.29048	0.00084
465	2.85	10.08	0.38739	0.00083
525	2.20	10.73	0.42972	0.00082
				0.00076

The coefficient is seen to be low, but nearly a constant. In this case, as in that of the ferrous sulphate, the mixture became slightly turbid on heating.

ZINC SULPHATE.

It is practically difficult to secure a good preparation of zinc sulphate crystallized without the addition of a trace of sulphuric acid. In absence of the acid crystallization is very slow. The preparation used below was made from a chemically pure commercial sample, by crystallizing with a trace of acid first and then from pure water, after heating the solution with pure zinc. The final crystallization to secure fifty grams required weeks for its completion. In my former paper attention was called to the fact that inversion with zinc sulphate is very slow, which is well shown below. The experiment was closed when the sugar was

about half inverted, and as the coefficient is not regular, it is not possible to estimate accurately the mean rate for the whole period.

EXPERIMENT 9.

$ZnSO_4.7H_2O.$ $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 17.94 grams of the sulphate.

$A = 17.25.$

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	13.10°	....	......	......
15	12.88	0.22°	0.00558	0.00037
45	12.35	0.75	0.01935	0.00043
105	11.34	1.76	0.04674	0.00044
165	10.40	2.70	0.07393	0.00045
285	8.48	4.62	0.13539	0.00048
405	6.51	6.59	0.20903	0.00052
525	4.68	8.42	0.29083	0.00055

MANGANOUS SULPHATE.

After several attempts a salt was obtained crystallized from perfectly neutral solution. Some of the crystals were so irregular in outline that it was not possible to determine from inspection whether they contained four or five molecules of water. Determination of SO_4 in the product showed, however, that a very small amount only of the latter salt was present. In making the solutions I assumed for convenience that the compound had the formula $MnSO_4.4H_2O$, and weighed out accordingly.

As I pointed out in my former paper, a solution of manganous sulphate and sugar undergoes a peculiar decomposition when heated, in which a very fine dark substance is thrown out from solution. The amount of this is so small that I could not collect enough for tests, in the work done, but it is still sufficient to make the polarimeter readings very difficult. All solutions had to be filtered before examination, but even with this precaution the readings were often obscure.

EXPERIMENT 10.

$MnSO_4.4H_2O$, $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 13.94 grams of sulphate.

$A = 34.80$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.50°	....	......	......
45	26.33	0.17°	0.00213	0.000047
75	26.15	0.35	0.00439	0.000058
135	25.76	0.74	0.00934	0.000069
195	25.05	1.45	0.01848	0.000095
315	22.33	4.17	0.05543	0.000176
435	19.84	6.66	0.09226	0.000212
555	16.75	9.75	0.14277	0.000257

EXPERIMENT 11.

$MnSO_4.4H_2O$. N.

In 250 cc., fifty grams of sugar + 27.88 grams of sulphate.

$A = 34.75$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.45°	....	......	......
15	26.25	0.20°	0.00250	0.00017
45	26.00	0.45	0.00566	0.00013
75	25.75	0.70	0.00883	0.00012
135	24.90	1.55	0.01981	0.00015
195	23.00	3.45	0.04541	0.00023
315	18.20	8.25	0.11770	0.00037
435	14.45	12.00	0.18397	0.00042
555	9.50	16.95	0.29053	0.00052

EXPERIMENT 12.

$MnSO_4.4H_2O$. $2N$.

In 250 cc., fifty grams of sugar + 55.76 grams of sulphate.

$A = 34.42$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.12°	....	......	......
30	25.12	1.00	0.01280	0.00043
90	22.80	3.32	0.04405	0.00049
150	17.82	8.30	0.11984	0.00080
220	12.33	13.79	0.22231	0.00101
338	4.60	21.52	0.42622	0.00126
450	0.27	25.85	0.60383	0.00134
570	—3.80	29.92	0.88360	0.00155

EXPERIMENT 13.

$MnSO_4.4H_2O$. $3N$.

In 250 cc., fifty grams of sugar + 83.64 grams of sulphate.

$$A = 34.00.$$

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	25.70°	....	....	....
30	24.22	1.48°	0.01933	0.00064
90	18.76	6.94	0.09915	0.00110
150	11.50	14.20	0.23481	0.00156
220	4.75	20.95	0.41587	0.00189
338	—2.69	28.39	0.78252	0.00232
450	—6.25	31.96	1.22185	0.00272
570	—8.05	33.75	2.13354	0.00363

The rates of inversion cannot be directly compared in the above experiments because the latter were not carried to completion. In the first case over one-third of the sugar originally present was inverted, in the second case almost exactly one-half, in the third case about six-sevenths, while in the last case the inversion was very nearly complete. By plotting the results it is possible to determine approximately the rate of inversion when just one-half of the sugar has been inverted and this I have done. The results are given below, and show that the coefficients, K, are nearly proportional to the concentrations, these being referred to that of the half-normal solution as unity.

Conc.	K.
1	(0.00032)
2	0.00054
4	0.00109
6	0.00172

The first coefficient, 0.00032, is uncertain because it was found by a rather wide extrapolation, but between the others there is fair agreement.

MANGANOUS CHLORIDE.

The salt used was purified by several crystallizations from the best obtainable Schuchardt product.

EXPERIMENT 14.

$MnCl_2.4H_2O$. $\frac{N}{4}$.

In 250 cc., fifty grams of sugar + 6.18 grams of chloride.

$A = 35.00$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.70°	....	....	....
15	26.60	0.10°	0.00124	0.00009
45	26.30	0.40	0.00499	0.00011
75	26.00	0.70	0.00878	0.00012
135	25.25	1.45	0.01838	0.00014
255	22.66	4.04	0.05327	0.00021
375	18.75	7.95	0.11190	0.00030

The high initial rotation here is very extraordinary, corresponding to a specific rotation of 66.75°.

EXPERIMENT 15.

$MnCl_2.4H_2O$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 12.35 grams of chloride.

$A = 34.84$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.54°	....	....	....
15	26.45	0.09°	0.00113	0.00008
45	26.16	0.38	0.00476	0.00011
75	25.85	0.69	0.00869	0.00012
135	24.52	2.02	0.02594	0.00019
255	22.26	4.28	0.05693	0.00022
375	17.15	9.39	0.13639	0.00036
495	13.00	13.54	0.21370	0.00043
555	11.52	15.02	0.24498	0.00044

EXPERIMENT 16.

$MnCl_2.4H_2O$. N.

In 250 cc., fifty grams of sugar + 24.70 grams of chloride.

$A = 34.63$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.33°	....	....	....
15	26.12	0.21°	0.00264	0.00018
30	25.86	0.47	0.00593	0.00020
60	25.15	1.18	0.01505	0.00025
120	23.05	3.28	0.04321	0.00036
180	20.07	6.26	0.08659	9.00048
300	15.60	10.73	0.16105	0.00054

EXPERIMENT 17.

$MnCl_2.4H_2O$. $2N$.

In 250 cc., fifty grams of sugar + 49.40 grams of chloride.

$A = 34.18$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	25.88°	....	....	....
15	25.38	0.50°	0.00640	0.00043
45	23.91	1.97	0.02578	0.00057
75	22.21	3.67	0.04933	0.00065
135	18.25	7.63	0.10971	0.00081
195	14.80	11.08	0.17016	0.00087
345	5.25	20.63	0.40183	0.00116

No very plain relation can be found connecting these rates of inversion. The coefficients corresponding to the time of completion of one-third of the inversion are here given.

Conc.	K.
1	(0.00038)
2	0.00041
4	0.00055
8	0.00088

The first coefficient had to be estimated and is uncertain.

FERROUS CHLORIDE.

Considerable difficulty was experienced in preparing a solution of ferrous chloride devoid of traces of free acid. A weighed excess of pure iron wire was covered with water in a small flask and then the calculated volume of titrated hydrochloric acid was added in amount just sufficient to produce the solution of required strength. The mixture was gently warmed and allowed to stand a short time. Warming was repeated at intervals through several hours, until the liberation of hydrogen became very feeble. The solution so obtained stood five days in the presence of the excess of iron, being boiled twice in the interval, and was then filtered cold into the sugar solution, which was made up to the proper volume with fresh distilled water.

The actual strength of solutions made in this manner was determined by titration later. The two following were almost exactly normal and half-normal.

Both solutions became turbid on heating and had to be fil-

tered before polarization for the first tests. After the lapse of about two hours the cloudiness disappeared and the solutions then taken from the thermostat were clear enough for direct polarization.

EXPERIMENT 18.

$FeCl_2$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 7.925 grams of chloride.

$A = 16.18$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	12.03°	....	....	....
15	9.47	2.56°	0.07507	0.00500
45	7.44	4.59	0.14517	0.00322
105	5.00	7.03	0.24783	0.00236
165	3.83	8.20	0.30725	0.00186
285	1.90	10.13	0.42749	0.00150
405	—0.50	12.53	0.64696	0.00160
525	—2.01	14.04	0.87884	0.00167

EXPERIMENT 19.

$FeCl_2$. N.

In 250 cc., fifty grams of sugar + 15.85 grams of chloride.

$A = 15.71$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	11.56°	....	....	....
15	9.40	2.16°	0.06424	0.00428
45	6.88	4.68	0.15360	0.00341
105	4.75	6.81	0.24679	0.00235
165	3.56	8.00	0.30913	0.00188
285	1.15	10.41	0.47190	0.00165
405	—1.42	12.98	0.76002	0.00187
525	—3.25	14.81	1.24194	0.00236

These results are very surprising, inasmuch as they show but little difference between the rates for the two concentrations. In both instances the rates rapidly decrease from the beginning and after the sugar has been about half inverted they increase a little. I give next some results from solutions which had not been boiled so thoroughly, and which may have held a little free acid.

EXPERIMENT 20.

$FeCl_2$. 0.52*N*.

In 250 cc., fifty grams of sugar + 8.242 grams of chloride.

$$A = 34.00.$$

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	25.70°	....	....	....
15	20.00	5.70°	0.07969	0.00531
45	12.80	12.90	0.20720	0.00460
75	9.00	16.70	0.29343	0.00391
105	6.19	19.51	0.37041	0.00353
165	2.42	23.28	0.50129	0.00304
285	—1.95	27.65	0.72771	0.00256
345	—3.96	29.66	0.89399	0.00258
405	—5.30	31.00	1.05436	0.00260

EXPERIMENT 21.

$FeCl_2$. 0.98*N*.

In 250 cc., fifty grams of sugar + 15.53 grams of chloride.

$$A = 33.60.$$

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	25.30°	....	....	....
15	19.84	5.46°	0.07702	0.00513
45	14.20	11.10	0.17416	0.00387
75	11.80	13.50	0.22314	0.00297
105	9.88	15.42	0.26675	0.00254
165	7.65	17.65	0.32358	0.00196
285	1.45	23.85	0.53734	0.00188
345	—1.50	26.80	0.69383	0.00201

The effect of free acid is not apparent. Six other experiments were made with normal and half-normal ferrous chloride solutions, the results of which were very similar to those above. In all cases the constant was found to increase before the completion of the inversion.

The constant for 0.001 *N* hydrochloric acid was determined for comparison at the same temperature, $t = 85°$, and with the same amount of sugar. It was found

$$K = 0.0051.$$

FERROUS BROMIDE.

Solutions of this salt were made by adding the proper amount

of bromine to an excess of iron and water. A reaction soon begins which is hastened by heat. Finally the solution is thoroughly boiled, which eliminates all free bromine and leaves the iron in the ferrous condition. It is then filtered into the cold sugar solution and is ready for use. A solution so made is practically neutral.

EXPERIMENT 22.

$FeBr_2$. 0.54 *N*.

In 250 cc., fifty grams of sugar + 14.58 grams of bromide.

$A = 31.43$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	23.13°	....	....	....
15	16.76	6.37°	0.09836	0.00655
45	9.76	13.37	0.24062	0.00534
75	6.07	17.06	0.33988	0.00453
105	4.00	19.13	0.40743	0.00388
165	0.68	22.45	0.54406	0.00329
285	—4.03	27.16	0.86691	0.00304
345	—5.60	28.73	1.06598	0.00309

EXPERIMENT 23.

$FeBr_2$. 1.04 *N*.

In 250 cc., fifty grams of sugar + 28.08 grams of bromide.

$A = 29.50$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	21.20°	....	....	....
15	13.60	7.60°	0.12938	0.00862
45	6.22	14.98	0.30785	0.00684
75	2.90	18.30	0.42060	0.00561
105	0.75	20.45	0.51317	0.00489
165	—2 70	23.90	0.72163	0.00437
285	—6.35	27.55	1.17979	0.00414
345	—7.50	28.70	1.56673	0.00454

The normal solutions here invert but little faster than the half-normal. The rates in both cases diminish rapidly from the start, but after the middle of the inversion become nearly constant, as was observed with the ferrous chloride. The first three of the solutions taken from the thermostat had to be filtered before polarizing.

FERROUS IODIDE.

A half-normal solution was made by mixing 15.87 grams of iodine with an excess of iron and water, in the usual manner. On complete disappearance of the iodine the solution was boiled and filtered into a cold sugar solution. Water was finally added to make the volume up to 250 cc. The amount of sugar present is not sufficient to prevent some decomposition on heating, but, as in the other cases referred to, the turbidity at first noticed disappeared after longer warming in the thermostat. The first polarizations were made after filtering, and those later were made directly.

EXPERIMENT 24.

FeI_2. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 19.37 grams of iodide.

$A = 32.03$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	23.73°	....	....	....
15	17.45	6.28°	0.09478	0.00632
30	13.57	10.16	0.16571	0.00552
45	11.62	12.11	0.20627	0.00458
60	9.73	14.00	0.24956	0.00416
90	7.50	16.23	0.30690	0.00341
150	4.40	19.33	0.40176	0.00268
270	0.90	22.83	0.54177	0.00200
390	—2.80	26.53	0.76520	0.00196

In my former paper a preliminary experiment with ferrous iodide was described in which the coefficient appeared to be nearly constant and much smaller than here. The experiments are, however, not comparable, as in the former case the sugar solution was very strong, containing, in 250 cc., 125 grams of sugar. In such a solution the degree of dissociation of the iodide would be necessarily very different from that in a weaker solution. In the strong solution no separation of ferrous hydroxide or other compound appears, even on warming. A strong syrup is much more stable than a weak one, and the lower rate of inversion may be thus easily accounted for.

CADMIUM CHLORIDE.

One solution of cadmium chloride was tested as to its inverting power. It was made with a salt purified by several crystallizations at a low temperature, free from uncombined acid.

EXPERIMENT 25.

$CdCl_2$. 0.94N.

In 250 cc., fifty grams of sugar + 42.958 grams of chloride.

$A = 29.71$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	21.41°	....	......	......
15	12.80	8.61°	0.14862	0.00990
30	6.59	14.82	0.30001	0.01000
60	−1.33	22.74	0.62967	0.01049
90	−4.89	26.30	0.94015	0.01044
150	−7.70	29.11	1.69475	0.01129

The rate of inversion is about as rapid as with 0.002N hydrochloric acid at the same temperature and same sugar concentration.

LEAD NITRATE.

A single test was made with a solution containing lead nitrate. The salt was recrystallized from a pure Schuchardt specimen and was weighed in proper amount directly.

EXPERIMENT 26.

$Pb(NO_3)_2$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 20.65 grams of uitrate.

$A = 33.70$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	25.40°	....	......	......
15	22.86	2.54°	0.03403	0.00227
45	17.38	8.02	0.11803	0.00262
75	12.10	13.30	0.21800	0.00284
135	2.28	23.12	0.50314	0.00372
195	−3.63	29.03	0,85831	0.00440
345	−7.70	33.10	1.74948	0.00507

The coefficient here is found to increase very rapidly, as was noticed by Walker and Aston in their experiments,[1] which were

[1] *Loc. cit.*

carried out with a half normal nitrate solution at 80°, but with a weaker sugar solution. The mean value they give from the results of polarization at three intervals is 0.00159, but the inversion was not carried nearly to completeness, as in the above case.

The experiments given show in a marked manner the extreme variations in the value and constancy of the inversion coefficient and the data obtained may be roughly tabulated as follows:

Potassium alum	*K* constant.		
Ferrous sulphate	"	increases	slowly.
Ammonium ferrous sulphate	"	"	"
Zinc sulphate	"	"	"
Cadmium chloride	"	"	"
Manganous sulphate	"	"	rapidly.
Manganous chloride	"	"	"
Lead nitrate	"	"	"
Ferrous chloride	"	decreases	rapidly.
Ferrous bromide	"	"	"
Ferrous iodide	"	"	"

In the cases of the last three salts the values of *K* decrease very rapidly at the beginning of the heating, but become nearly constant later, finally, in fact, appearing to increase a little. This behavior seems to bear some relation to the stability of the salts in aqueous or weak saccharine solution. As was mentioned these ferrous halogen solutions became turbid in the thermostat, and the first three or four portions withdrawn in each case for polarization had to be filtered. Later, the liquids became perfectly clear under the influence of longer heating.

During the turbid stage of the reaction, owing to the temporary separation of a trace of base in insoluble form, the amount of free acid present would be relatively increased, and would therefore greatly accelerate the speed of inversion. With the clearing of the solutions on longer heating the normal hydrolysis only would obtain and then the reaction should approach in regularity that due to the presence of a small constant amount of mineral acid.

It was mentioned that the solutions with ferrous sulphate and ferrous ammonium sulphate became likewise turbid on heating. But here the very slight opalescence persisted through the

whole time of heating, and was perhaps greater at the end of the reaction than at the beginning. Other experiments also show in this respect a marked difference between ferrous sulphate and chloride. In my former paper I referred to solutions of these salts which had been used qualitatively. Portions of these solutions that had not been heated are still in existence. After standing eight months in the light I find that the chloride is practically clear, while the sulphate has become much changed. The bottle contains a decided flocculent precipitate. My former experiments with a strong solution seemed to indicate that at a temperature of 100° the first slight precipitate which forms disappears, but this is not true of the weaker solutions at 85°.

The slight precipitate of ferrous chloride and other halogen compounds being temporary, while that of ferrous sulphate is apparently permanent, we should expect just such irregularities in the speed of inversion, as the experiments actually show. A solution of manganous sulphate with sugar becomes also slightly decomposed on heating, and the decomposition increases with the time and temperature. At a temperature of 100° a solution of fifty grams of sugar and ten grams of the sulphate in 100 cc. becomes so dark that an exact polarization is not possible, even after filtering. The solution in the present case is much less concentrated, but the precipitate is still marked and its formation is undoubtedly attended by the separation of a little free acid. We should therefore expect an acceleration in the rate of inversion as before.

These considerations do not aid us in explaining, however, the increase in K for manganous chloride, cadmium chloride or lead nitrate. The solutions with these salts are clear and remain so throughout the reaction. In the case of manganous chloride it must be remembered that an almost complete loss of color follows after heating. The pink fades, and in a few hours at the temperature of the thermostat becomes imperceptible in a small volume of the liquid. The color is not restored by cooling. We have here evidently a reaction in which a change takes place in the form of combination of the manganese, with a necessary alteration in the degree of dissociation of the salt.

It is true, as already said, that most of the bases under consideration form compounds with the sugars, so that we should expect from this cause a slight disturbance at least in the apparent rate of inversion. Too little is known of the optical properties of these saccharose, dextrose and levulose metallic compounds to say just what effect they would have on the rotation, but that they have some action is suggested by the results of some of the polarizations to determine the end point in the inversion. This was usually found a little below the theoretical, —8.6° for a 200 mm. tube, but in several cases it was found above after prolonged heating. This was also true of a solution of sugar with manganous chloride, which stood exposed to the light several months.

It must be remembered also that solutions of dextrose are easily oxidized, and those of levulose much more so. The dark color often seen near the end of the reaction, points to such a decomposition.

It will be recognized that a determination of the hydrolysis of many of the heavy metallic salts cannot be measured with great accuracy, because of these several disturbing influences, but a comparison of some little value in the above cases may be made by considering the results obtained at the beginning of the reactions in which the coefficient is an increasing one, and near the end of the reaction in cases where it decreased and then became nearly constant. By taking the mean of the first two values in the one case, aud of the last two in the other, we obtain the second column of the table below as the most probable values of the coefficient for half-normal solutions.

In the third column is given a calculation of the extent of hydrolysis of the salts, expressed in per cents. of total salt present, and based on a comparison with hydrochloric acid acting in 0.001 normal solution at the same temperature on same amount of sugar. This comparison is at best a rough one, assuming as it does complete hydrolysis of the acid, and neglecting the effect of the excess of undecomposed salts on the rate of inversion.

	K.	Salt hydrolyzed in per cent.
Lead nitrate	0.00244	0.096
Manganous chloride	0.00095	0.035
Manganous sulphate	0.00052	0.020
Ferrous sulphate	0.00085	0.033
Ferrous ammonium sulphate	0.00068	0.026
Zinc sulphate	0.00040	0.016
Ferrous chloride	0.00164	0.063
Ferrous bromide (0.54N)	0.00300	0.109
Ferrous iodide	0.00198	0.078
Potassium aluminum sulphate, $\frac{N}{4}$	0.01835	1.440
Cadmium chloride 0.94N	0.01000	2.080

The amount of hydrolysis is small in all cases except those of the alum and cadmium chloride.

My thanks are due to Mr. S. R. Macy for much assistance in the experimental work of the above.

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DETERMINATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK BY THE AMMONIUM ACETATE METHOD.

BY THOMAS S. GLADDING.

Received June 30, 1896.

THE oldest method of separating alumina and iron phosphates from lime phosphate is, probably, the ammonium acetate method. This has been severely criticised, and just at present seems to be under condemnation. The following investigation has convinced the writer that, when properly carried out, not only does the method give an accurate separation of iron and alumina from lime phosphate, but also gives a neutral phosphate of uniform composition from which the iron oxide and alumina present may be accurately estimated.

In brief, the method used is this. If a weakly acid solution of phosphates of iron and alumina together with a large amount of calcium phosphate be slowly poured into a strong solution of ammonium acetate made acid with acetic acid, the iron and alumina are precipitated as phosphates, upon digestion for a short time at a gentle heat. This precipitate, however, con-

tains more or less calcium phosphate, which is removed by several reprecipitations. I shall demonstrate by experiment:

First, That upon continued reprecipitations of iron and alumina as phosphates in this manner, there is no appreciable diminution of the quantity of either finally obtained, provided there always be a large excess of phosphoric acid present.

A standard solution was made by dissolving twenty grams of ammonia alum (C. P.) in distilled water. This was slightly acidified with hydrochloric acid, in order to prevent the alumina from separating on standing, and diluted to one liter. This solution, upon being standardized, was found to contain the theoretical amount of alumina, that is,

$$\text{Ten cc.} = 0.0225 \text{ grams } Al_2O_3.$$

One precipitation, in the manner described above, of the alumina in ten cc. gave

	$Al_2O_3.P_2O_5$, found.	Al_2O_3.
1	0.0545	0.0228
2	0.0549	0.0229
3	0.0546	0.0228
4	0.0540	0.0226
5	0.0545	0.0228

Three successive precipitations, in which one gram of ammonium phosphate was added before each precipitation, gave

	$Al_2O_3.P_2O_5$.	Al_2O_3.
1	0.0550	0.0230
2	0.0547	0.0229
3	0.0544	0.0227

Five successive precipitations were also tried under the same conditions, with the following results:

	$Al_2O_3.P_2O_5$.	Al_2O_3.
1	0.0536	0.0224
2	0.0530	0.0222

When, however, the excess of phosphoric acid was omitted before the reprecipitations, there was a loss of alumina.

An iron solution was made by dissolving C. P. iron wire in hydrochloric acid and oxidizing it with nitric acid. When carefully standardized it was found that

$$\text{Ten cc.} = 0.0296 \ Fe_2O_3.$$

Three successive precipitations, adding one gram ammonium phosphate before each, gave

	$Fe_2O_3.P_2O_5$.	Fe_2O_3.
1	0.0545	0.0289
2	0.0550	0.0291
3	0.0548	0.0290

Five successive precipitations, in the same way, gave

	$Fe_2O_3.P_2O_5$.	Fe_2O_3.
1	0.0550	0.0291
2	0.0560	0.0297

Second. That upon three successive precipitations in the presence of a large amount of calcium phosphate, as is the case in the analysis of rock phosphate, the precipitate of the phosphates of iron and alumina is sufficiently pure to be taken as such. Of the standard solutions, five cc. of each would together give a precipitate of combined phosphates about equal to that usually found in one gram of phosphate rock. The mixture so analyzed was made up as follows:

Five cc. alumina solution = 0.01125 Al_2O_3.
Five cc. iron solution = 0.01480 Fe_2O_3.
0.7000 grams calcium phosphate.

This was given three precipitations, the excess of phosphoric acid being supplied before the second and third precipitations.

	Phosphates obtained.	Al_2O_3 obtained.	Fe_2O_3 obtained.
1	0.0552	0.0115	0.0146
2	0.0540	0.0110	0.0146
3	0.0537	0.0109	0.0146
4	0.0536	0.0109	0.0146

The iron oxide was determined by volumetric method in the ignited precipitate and the alumina by subsequent calculation.

In addition twenty cc. alumina solution containing 0.0450 grams Al_2O_3, together with 0.700 grams calcium phosphate, were given three successive precipitations in the same way with the following results:

	$Al_2O_3.P_2O_5$ obtained. Grams.	Al_2O_3 obtained. Grams.
1	0.1092	0.0456
2	0.1074	0.0449

In order to prove that the aluminum phosphate precipitated was the normal phosphate, the ignited precipitates were fused, and the phosphoric acid in them estimated.

	$Al_2O_3.P_2O_5$.	P_2O_5 obtained.	Al_2O_3 by diff.	Al_2O_3 by calc.
1	0.0538	0.0313	0.0225	0.0225
2	0.0533	0.0312	0.0221	0.0223

The phosphate of alumina is multiplied by the factor 0.418 to obtain the alumina.

Therefore, in determining iron oxide and alumina in phosphate rocks proceed as follows:

Four grams of the finely ground sample, previously freed by a magnet from any metallic iron derived from the iron mortar used in grinding the sample, are digested for half an hour, at a temperature just below the boiling-point, with about thirty cc. dilute hydrochloric acid (1-1). This will prevent the solution of any pyrites if present. Filter and wash thoroughly into a 200 cc. flask, add a little nitric acid, and boil to oxidize the iron, cool, and fill to mark with water. Take two portions, fifty cc. = one gram, twenty-five cc. = one-half gram, and proceed with each as follows:

Almost neutralize the solutions with strong ammonium hydroxide until the precipitate formed dissolves with difficulty, and thoroughly cool by placing the beaker in a dish of cold water. The neutralization is then completed by carefully adding dilute ammonium hydroxide until the precipitate remains permanent, then just dissolve by adding dilute hydrochloric acid, drop by drop, stirring well. Have ready in another beaker a mixture of fifteen cc. of a strong solution of ammonium acetate (made by neutralizing thirty per cent. acetic acid with strong ammonium hydroxide) and five cc. of acetic acid. Carefully pour the cold faintly acid solution of phosphates in a fine stream into this mixture, stirring all the while. Digest at 60° C. from one-half hour to one hour, until the supernatant liquid is clear and the flocculent precipitate is well settled to the bottom.

Filter and wash the precipitate once with a ten per cent. ammonium acetate solution, merely rinsing out the beaker in which the precipitation was made. Dissolve the precipitate from the paper into the same beaker with a few cubic centimeters of hot dilute hydrochloric acid (1-4). Use as little acid as possible in order to keep the bulk of the solution small. Add one gram of ammonium phosphate, neutralize with ammonium

hydroxide and add hydrochloric acid until the precipitate just dissolves as before and pour into a mixture of fifteen cc. ammonium acetate solution and five cc. acetic acid. Digest at 60° C. for one-half to one hour and filter, and wash once with the ten per cent. ammonium acetate solution. Redissolve and repeat the precipitation, being careful to again add one gram of ammonium phosphate to the solution, in order that there be a sufficient excess of phosphorus pentoxide to precipitate all the alumina as a neutral phosphate. Wash the precipitate three times with dilute ammonium acetate solution.

Take the filter, while wet, from the funnel and ignite in a tared platinum capsule, using a very low flame until the filter paper is thoroughly charred. The heat is increased gradually until the paper is completely consumed, and finally the blast lamp is used for a minute. Weigh as combined phosphates of iron and alumina. The iron is determined volumetrically in the solution of the weighed precipitates. The iron oxide present in the rock is also determined separately by volumetric process, preferably the bichromate method, in a solution of five grams of the rock in dilute hydrochloric acid (1-1), reducing all iron to protoxide and titrating with bichromate.

The ignited precipitate from one of the duplicate precipitations may, if desired, be dissolved and subjected to a fourth precipitation and the filtrate tested for lime by adding ammonium oxalate and heating. My thanks are due to our assistant, Thomas Brown, Jr., for valuable aid in the above analytical determinations.

LABORATORY OF STILLWELL & GLADDING,
NEW YORK CITY.

A NEW METHOD FOR THE ESTIMATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK.

BY THOMAS S. GLADDING.

Received June 30, 1896.

THE method for the separation of alumina from phosphate of lime by three successive precipitations with ammonium acetate is tedious, though accurate if proper precautions be taken, as shown in the preceding paper on this subject.

The following modification suggested itself as saving both

time and labor. This modification consists of the separation of alumina from calcium phosphate and iron by means of its solubility in an excess of caustic potash. To demonstrate the accuracy of this method, a solution of ammonia alum, twenty grams in a liter, was used as in the previous experiments, ten cc. containing 0.0225 grams Al_2O_3. The caustic potash solution was made by dissolving 500 grams of caustic potash in distilled water and diluting to one liter. Chemically pure caustic potash, purified by barium, was used and was carefully tested for alumina, as much so-called chemically pure potash contains an appreciable amount of alumina.

To a solution of mixed phosphates of alumina, iron, and lime were added fifteen cc. of the C. P. potash solution. The mixture was digested for an hour at a temperature of 70° C., with occasional stirring. It was then filtered, the filtrate neutralized with hydrochloric acid, and the alumina was precipitated as a phosphate with ammonium acetate as described in my ammonium acetate method.

Ten cc. standard alumina solution + 0.030 gram iron oxide + 0.500 gram calcium phosphate gave

	$Al_2O_3.P_2O_5$ found. Grams.	Al_2O_3. Grams.
1	0.0538	0.0225
2	0.0542	0.0227
3	0.0543	0.0227
4	0.0543	0.0227

Comparative tests were made on phosphate rocks between this method by solution in C. P. potash and by three successive precipitations with ammonium acetate.

	By new potash method. Al_2O_3 found. Per cent.	By acetate method. Al_2O_3 found. Per cent.
1	1.05	1.03
2	1.19	1.16
3	1.86	1.61
4	1.07	0.99
5	1.88	1.98

These results show the accuracy of this method, both in obtaining a known amount of alumina and in showing close agreement with results by the acetate method.

This method has been in use in our laboratory for over a year. A reprint of an article by M. Henri Lasne[1] has just been received, giving a method for the separation of alumina from phosphates of iron and lime very similar to this. M. Lasne uses caustic soda instead of potash and precipitates his aluminum phosphate with ammonium hyposulphite instead of ammonium acetate. I have made a few comparative tests by my method and that of M. Lasne and find closely agreeing results.

Using ten cc. standard alumina solution + 0.500 grams calcium phosphate I found

	By my method.		By Lasne's method.	
	$Al_2O_3.P_2O_5$. Grams.	Al_2O_3. Grams.	$Al_2O_3.P_2O_5$. Grams.	Al_2O_3. Grams.
1	0.0542	0.0220	0.0540	0.0226
2	0.0538	0.0225	0.0533	0.0223

In the analysis of a phosphate rock I found

By my method. Al_2O_3 found. Per cent.	By Lasne's method. Al_2O_3 found. Per cent.
1.75	1.73
1.80	...

The detailed method used in my work is as follows: Treat the finely ground rock phosphate with a magnet to remove any metallic iron derived from the iron mortar used in the preparation of the sample. Dissolve four grams of the rock in thirty cc. dilute hydrochloric acid (1–1), heating just below the boiling-point for half an hour. This prevents the solution of pyrites. Filter into a 200 cc. flask, add a few drops of nitric acid, and boil to oxidize the iron, cool and dilute to mark. Take fifty cc. containing one gram of rock and run into twenty cc. of the solution of C. P. caustic potash. Digest for an hour at 70° C., stirring occasionally. Let the precipitate settle and filter on a large paper, first decanting the supernatant liquid on the paper and finally washing on the precipitate. Wash two or three times with hot water.

To the filtrate add one gram of ammonium phosphate, acidify with hydrochloric acid, add ammonia until a permanent precipitate is formed and dilute hydrochloric acid, drop by drop, until it is just dissolved. Add a mixture of fifteen cc. neutral ammo-

[1] From the *Bulletin de la Société chimique de Paris*, [3] 15, 118, *1896*.

nium acetate solution and five cc. acetic acid (thirty per cent.) and digest for half an hour at 70° C., by which time the precipitation is complete.

Filter, washing five or six times with hot ammonium acetate solution (ten per cent.), stirring up the precipitate with the jet each time. Ignite with a low flame until the paper is charred, increase the heat, and, when the paper is completely consumed, blast for a minute. The precipitate is the normal aluminum phosphate and its weight multiplied by the factor 0.418 gives the Al_2O_3.

The iron oxide is determined volumetrically, preferably by the bichromate method, in a solution of the precipitate of iron oxide and calcium phosphate thrown down by the caustic potash. It is also determined separately, by the same method, in a solution of five grams of the rock in dilute hydrochloric acid (1–1).

My thanks are due to Mr. H. E. Cutts, A.M., for valuable assistance in the above investigation.

LABORATORY OF STILLWELL & GLADDING.
NEW YORK CITY.

SOME THOUGHTS ABOUT LIQUIDS.

BY CLARENCE L. SPEYERS.

Received June 3, 1896.

CONSIDER an empty closed space. Imagine a quantity of liquid put into it, enough to fill the space with vapor and leave some liquid over. A portion of the liquid changes into vapor and passes into the previously empty space above the liquid and continues doing so until the pressure of the vapor reaches a certain value, when the vaporization ceases.

The usual way of explaining this vaporization starts out by assuming that, with the exception of the surface, the liquid is perfectly homogeneous in a physical sense. That is, there is not a single particle of the liquid which for any appreciable length of time is different from any other particle, but of course, spaces between the particles of liquid are recognized. At the surface of the liquid, however, a distinction is to be made. For outside the surface, the activities are different from those within the surface, otherwise there would be no boundary. So that the

particles at the surface are subjected to activities that are different in different directions, and consequently the particles so situated will behave differently from those particles entirely within the liquid.

In van der Waal's theory the mutual attractions of the particles of the liquid are considered as the restraining force to keep the particles more or less together. This assumed force must be very great—a good many hundred atmospheres. Inside the liquid, below the surface, the attraction is equal in all directions, but at the surface it acts only in one direction, inwards, normal to the surface. Now, although the force restraining the particles of liquid from separating is so great, yet the theory of common acceptance assumes that some particles do break away from the mass of the liquid and form vapor. The liquid is said to evaporate. It is hard to accept this view of the case, particularly as electrical results point towards an exceedingly quiet condition of affairs within the body of liquids.

Still admitting that the particle does break away from this attraction, it cannot do so without an abundant supply of energy, which must be accounted for. It does not seem right to find this energy in the heat of vaporization, for a particle of liquid will voluntarily take heat energy from the liquid to do this work, and so go off as a particle of vapor at the sacrifice of the energy of the liquid.

It is not possible to prevent a liquid from vaporizing by refusing to give it heat; it will take the required heat from the rest of the liquid. In other words, the condition of the liquid state strongly favors vaporization.

The common theory tries to get over this difficulty by claiming that the particle which gets away, gets away by virtue of an inherent kinetic energy greater than the attractic energy of the particies of liquid, that is, greater than the force denoted by van der Waal by $K = \frac{a}{v^2}$, and that it possesses this excess of kinetic energy in the body of the liquid, before it got away, and that it got away only by virtue of this excess of kinetic energy. Similarly with all particles in the liquid having a kinetic energy

greater than the energy of the mutual attraction of the particles the one for the other.

Still again admitting that the particles with the greater kinetic energy do succeed in getting out, we shall have to look for a loss in the mean kinetic energy of the liquid, to be shown by a fall in temperature. This is the case and in this respect theory and fact agree, for vaporization lowers the temperature of the liquid. In regard to the vapor, however, we meet with this difficulty. The kinetic energy of a given particle while within the liquid might be just sufficient to carry it beyond the sphere of action of the liquid, in which case the kinetic energy remaining to the particle after reaching freedom would be little and its temperature should be less than that of the liquid; on the other hand, the kinetic energy of the given particle might be far more than sufficient to carry it beyond the sphere of action of the liquid and then the kinetic energy that the particle still has after reaching freedom, should be more or less great. Consequently a particle of vapor, just after getting out of the liquid, might have any temperature between absolute zero and ∞°, in some cases perhaps touching the inferior limit, but of course, never reaching the superior limit. As a consequence of this we should expect to find the temperature of the vapor very different from that of the liquid; but this is not the case, observation has never shown that the temperature of the vapor is very different from that of the liquid which produces it. However, this is not a fatal objection, for we can assume that the mean of kinetic energy, while within the liquid, of the particles that escape from the liquid is of just such a value that after they have all got out of the liquid, the diminution of their mean kinetic energy, due to the attraction of the liquid, brings the kinetic energy left to them to the mean kinetic energy of the liquid. This seems like a forced explanation, very forced, but still perhaps not more so than the theory it is intended to help.

However, we are not yet out of the difficulty. For what becomes of the kinetic energy lost by the particles as they pass out into the vapor state?

So far as the liquid is concerned, it may take the form of heat energy and so lessen the quantity required to supply the deficit

due to the escape of the particles with great kinetic energy from the liquid. But all of the lost kinetic energy cannot be absorbed here in the liquid, some must also go into the vapor particles. It may take the form of heat, as we have suggested in the case of the liquid, but then we have to assume that the kinetic energy, while within the liquid, of the particles that escape is of just such a value that, after they have all got out of the liquid, the diminution in their mean kinetic energy, due to the attraction of the liquid plus this correction, brings the kinetic energy left to them to the mean kinetic energy of the liquid, which is absurd.

Nor does the attractive energy seem to be stored up as potential energy, as in the case of a stone raised above the surface of the earth, for there is no evidence at all that a vapor particle tends toward the liquid as the stone does toward the earth. When the particle gets out of the liquid it seems to be utterly indifferent to the liquid.

Of course the mutual attraction that all bodies have for each other is left out of account.

Nor is there any sign of electrical action, at least if the experiments made up to the present time are conclusive.

There are then a good many very serious objections to the present theory of vaporization.

First, in accounting for the escape of the vapor.

Second, in accounting for the temperature of the vapor.

Third, in accounting for the kinetic energy lost by the particle in getting through the surface of the liquid and beyond the sphere of action of the liquid particles.

Let us now turn our attention to another view of the case. Consider a liquid which has no vapor-tension of its own, a non-volatile liquid, but which can dissolve gases. The liquid and gas are supposed to act according to Henry's law, that is, the ratio of concentration of the gas in the liquid part and in the gaseous part is to be constant, or in other words, the quantity of gas dissolved by the liquid is to be proportional to the pressure on the gas.

In such a system there are three constituents to be considered. The gas in the gaseous state, the gas in solution, and the solvent.

The state of the dissolved gas is not positively known, but in all probability it is in a state corresponding to a gas under high pressure for these reasons. In the first place, it is hard to see how a substance like nitrogen, for example, could be in the liquid state in a solution of moderate concentration. Great pressure is required to liquefy it even when the temperature is far below the ordinary temperature, and at the ordinary temperature it has hitherto been found impossible to liquefy nitrogen, no matter how great the pressure. Still it would be consistent with the ordinarily accepted theory to claim that the attraction of the particles of solvent could overcome the great internal energy of the gas particles and bind them down to a lesser activity and produce the liquid state. But on the other hand, modern investigation has very plainly shown that dissolved substances have a gaseous nature; the particles of the dissolved body are free to assert their physical individuality. That is to say, the solvent is to be considered rather as a medium through which the dissolved body can be put under certain conditions, the conditions varying to some extent with each solvent, but all solvents having the common action of allowing a sort of gasification of the substance dissolved, In general the solvent is not to be considered as a substance which unites with the dissolved body, forming a new compound. For example, consider anhydrous calcium chloride. When this is treated with water there is strong evidence of combination of the two to form calcium chloride hydrate. If the quantity of water is properly adjusted the whole of it combines with the calcium chloride, forming a crystallized hydrate. If this crystalline substance is treated with more water, solution begins and during this process, which is the real solution, there is no sign of chemical action. It is true, some scientists, particularly those of the English school, have denied this and have claimed to find strong evidence of a chemical action during the process of solution, but so far all such claims have turned out to be mere opinions based upon very doubtful measurements.

So we are to look upon solution as being a change in which the dissolved body is gasified. Sometimes a further change, electrolytic dissociation, takes place, but that is outside the

scope of this article. It is in best accordance with what we know about other bodies to assume that the dissolved nitrogen is in the form of a gas, and to recognize two states in the solution, the gaseous state of the substance in solution and the liquid state of the solvent.

Let us now pass on to a liquid which gives off vapor. The purpose of this article is to justify the view that this vapor behaves toward the liquid just as the nitrogen did toward its solvent in the previous case, of course, with the obvious limitations due to identity in the composition of vapor and liquid.

The boundary dividing vapor from liquid is commonly supposed to be at the surface of the liquid, although the possibility of a differentiation occurring inside the liquid does not seem to be denied, for so far as could be found out by the writer, the question of such a possibility has never been raised.

The tendency for a liquid to vaporize and the pressure of its saturated vapor is evidently a function of temperature only. There seems to be no reason, therefore, why the fluid should not separate into vapor and liquid within the surface of the liquid. That it is possible for vapor to be there follows from what we know about the gaseous nature of the substances in solution. It is rather odd that this view of the case was not adopted at the outset by chemists.

According to this view, when we heat a liquid we increase the energy of translatory motion, we increase its temperature. But besides this we cause a separation of some of the liquid particles from the body of the liquid, bringing them into a state of freedom, such that they can behave just as the particles of any other substance would do in the same solvent. This of course will consume considerable energy. These free particles of vapor in the liquid we shall call dissolved vapor particles. So that on heating in liquid we produce dissolved vapor and raise the temperature of the whole fluid; possibly we do more, but at any rate we do these two things. Now by Clausius' theory of the true specific heat, the heat required to raise only the temperature of a unit mass of substance one degree, should be the same whatever the state of the substance may be, and the value of the true specific heat should be the value of the specific heat when

the substance is in such a state that the heat added can only change its temperature and not do any other internal work, namely when the substance is in a state of gas. So if we subtract from the specific heat of the liquid the specific heat of the gas, the remainder should be the heat consumed in other internal work, and if no other internal work is done than the rise in temperature and production of dissolved vapor, we should get the heat required to change some of the liquid into dissolved vapor. The quantity changed into vapor however is so far unknown.

The dissolved vapor is supposed to be produced until its energy balances the energy of the liquid part.

Suppose, for example, we heat one gram of water one degree in a closed vessel which does not allow it to give off gaseous vapor. The heat required will be about one calorie, depending upon the initial temperature; one calorie is near enough for our purpose. A part of the heat goes to increase the translatory motion and is the true specific heat; but another part, perhaps the whole of the remainder, we claim goes to produce dissolved vapor. Subtracting the true specific heat of water, namely the specific heat of water vapor at a high temperature = 0.4776, we have left 0.5224 as the heat required to change a certain unknown quantity of water into dissolved water vapor, provided that no internal work is done but the two kinds we have considered. We shall assume this to be true until there is evidence of a more complex change.

Now suppose a space be made over the liquid, to let a certain quantity, say one per cent., be changed into gaseous vapor. It is of course evident, if the theory be at all tenable, that the vapor arising from the liquid comes from the dissolved vapor and bears to the dissolved vapor the same relation that the nitrogen did to the dissolved nitrogen. Comparatively little heat should be required in this process, for most of the change has been effected in the body of the liquid. Whatever is required here should be looked upon as the true heat of vaporization; that which is usually so called we are to consider as including the heat required to change a unit mass of liquid into dissolved vapor as well as the heat required to vaporize the unit mass of dissolved

vapor. The two quantities should evidently be kept carefully separated.

Let us now proceed to determine the concentration of the dissolved water vapor. As the dissolved water vapor is supposed to be like a dissolved gas, Henry's law should give us some aid in finding the quantity. We might assume, in the first place, that the relative vapor density of a liquid at two different temperatures gives the relative osmotic pressures of the dissolved vapor at those temperatures, were it not for the uncertainty as to how the temperature affects the pressure of the vapor and the osmotic pressure of the dissolved vapor. It would not do to assume that each was affected in the same degree by a change in temperature. But our theory does allow us to claim in the case of a given liquid at a constant temperature that two different vapor-tensions will correspond to two different concentrations of the dissolved vapor by Henry's law, and that the relative vapor-tensions are as the relative concentrations of the dissolved vapor. Now we can change at will, within quite a wide range, the vapor tension of a liquid without changing its temperature and without introducing any complications.

To understand this let us refer back to the original conception of the dissolved vapor. If we have liquid water in a vessel with any number of gases under moderate pressure, the partial pressure of the saturated water vapor will be very nearly the same as if it alone were present in the space containing the gases. So when we dissolve a substance in water it would seem as if we might argue that the osmotic pressure of the dissolved substance should not affect the pressure of the dissolved water vapor. However the conditions in the two cases are very different. In the first case there is abundant space for the water vapor so that all that is necessary is time for the concentration of the water vapor to reach the same value no matter how many gases may be present, provided of course that the total pressure be not very great. When however the total pressure is great, the vapor-tension of the liquid diminishes very much. This is just the condition that holds in a liquid. The volume available for a dissolved substance is very small, and so anything put into this space will very materially lessen the space available for the dis-

solved vapor, particularly as the quantities used in solutions are generally very much greater than those used in the gaseous state.

Suppose we have n gram-molecules of a substance whose molecules do not dissociate on dissolving, say sugar, and dissolve it in water. Let ν be the number of gram-molecules of dissolved vapor after the n gram-molecules of substance have been dissolved, then the total number of gram-molecules present in solution will be $\nu + n$, and the relative number of gram-molecules of substance dissolved to total number of gram-molecules in solution is

$$\frac{n}{\nu + n}.$$

Now let j be the concentration of the dissolved vapor when alone in the liquid, and j' its concentration after the new substance has been added, in this case the sugar. $j - j'$ will be the decrease in the concentration of the dissolved water vapor due the addition of the n gram-molecules of sugar, and since a gram-molecule of all substances occupies the same volume, the decrease in concentration $j - j'$ will be the same whatever the substance dissolved may be, provided the same number of gram-molecules be taken in each case, or the decrease in concentration of the dissolved vapor is proportional to the number of gram-molecules dissolved in a certain fixed volume of solution. If the temperature is constant the concentration of the dissolved water vapor cannot rise above the value j, which it has when only dissolved vapor is present; when we try to get above this value the dissolved vapor turns to liquid water. Hence the number of gram-molecules in a unit volume must be fixed, if the temperature is constant, that is

$$\nu + n = \text{constant}.$$

We have, therefore,

$$\frac{j - j'}{j} = \alpha \frac{n}{\nu + n} \qquad (1)$$

where α is a constant.

$j - j'$ can be calculated by van't Hoff's law, and n is known, but the other quantities are not, so neither j or ν can be calculated from this equation.

There is however another relation that can be deduced.

The concentration of the dissolved vapor is measured by its osmotic pressure.

Let π, ϕ, be respectively osmotic pressure and osmotic volume of the dissolved vapor, when it alone is present; π', ϕ', the corresponding quantities when a substance is in solution; p, v, the pressure and volume of the vapor in contact with the pure solvent; p', v', the corresponding quantities when a substance is in solution.

Consider an isothermal reversible cycle composed of the following parts.

By means of a semipermeable diaphragm let a gram-molecule of dissolved vapor pass from the pure solvent, the work will be

$$-\pi\phi = -RT.$$

Let the gram-molecule of vapor expand until it has a pressure of π the work will be

$$-\int_{\pi'}^{\pi}\phi d\pi = -RTl\frac{\pi}{\pi'}.$$

Let it then pass into the solution; the work will be

$$+\pi'\phi' = +RT.$$

Let x gram-molecules pass out of the solution in the form of vapor; the work will be

$$-xp'v' = -xRT,$$

where x denotes the number of gram-molecules of gaseous vapor necessary to make one gram-molecule of dissolved vapor.

Let the x gram-molecules of vapor be compressed until the pressure equals p; the work will be

$$+x\int_{p'}^{p} vdp = +xRTl\frac{p}{p'}.$$

Let the x gram-molecules be driven into the pure solvent; the work will be

$$+xpv = +xRT.$$

Thus the cycle is completed. The quantity of solution is supposed to be so large that the addition and removal of the quantity of the solvent used in the cycle will have no appreciable effect upon the concentration of the solution.

The sum of the changes of energy must be zero, so

$$-RT - RTl\frac{\pi}{\pi'} + RT - xRT + xRTl\frac{p}{p'} + xRT = 0;$$

Hence,
$$\frac{\pi}{\pi'} = \left(\frac{p}{p'}\right)^x \tag{2}$$

We shall assume that x equals 1; there is no good reason for thinking otherwise, and the simplicity in the structure of dissolved bodies favors this assumption.

From the theory we have

$$\frac{j}{j'} = \frac{\pi}{\pi'} \tag{3}$$

We have therefore from 1 through 3 and 2,

$$1 - \frac{p'}{p} = \frac{p - p'}{p} = \alpha\frac{n}{\nu + n} \tag{4}$$

but from experiment,

$$\frac{p - p'}{p} = \frac{n}{N + n} \tag{5}$$

where N is the number of gram-molecules of liquid in which n gram-molecules of substance have been dissolved.

Hence,

$$\alpha\frac{n}{\nu + n} = \frac{n}{N + n} \tag{6}$$

Now as equation (6) is true for any small value of n it will be true for a value so small in comparison with ν and N, that it may be neglected, and so

$$\frac{\alpha n}{\nu} = \frac{n}{N},$$

or,

$$\alpha = \frac{\nu}{N} \tag{7}$$

Substituting in (6) we have

$$\frac{\nu}{N}\frac{n}{\nu+n}=\frac{n}{N+n},$$

or,

$$\nu=N \tag{8}$$

That is, the concentration of the dissolved vapor is the same as the concentration of the liquid, or in other words, all the solvent is to be considered as dissolved vapor.

This is very interesting, for it is in effect the same conclusion that van der Waals reached in his celebrated treatise, though he pursued a very different method.

It would seem from this result that matters were left in about the same state that they were in at the outset; that the view of dissolved vapor was no better than the old view, which claimed that the change into vapor took place only on the surface of the liquid. But we have really gained several things.

In the first place we have found that reasoning from the analogy that a dissolved gas and the same gas in contact with the solvent bears to the liquid and its vapor we got to the idea of dissolved vapor and from that to a result in agreement with a much older theory.

Secondly, we have found that a liquid is to be looked upon as a condensed gas, not simply condensed in the sense that it is a matter compressed into smaller space, but condensed in the sense that the gaseous activity, pressure, is carried into the liquid condition, and we are to treat a liquid as we would a gas.

Thirdly, it follows from this view that a substance dissolved is simply brought into the same condition that the liquid is in, and consequently should have the same property of exerting an osmotic pressure that the liquid has.

Finally, what causes the condensed gaseous state? Until this is answered the problem of liquid and gas is essentially unsolved. That it is due to an attraction between the molecules, is hardly possible, as we have seen at the beginning of this paper. Indeed so soon as we begin to reflect upon the complications that are introduced the moment the ideas of molecule and attraction are brought into an investigation, and these complications are all

the time increasing instead of diminishing, the more natural and simple appears the view of Ostwald that we shall find a better solution of such problems in energy alone, matter being only a collection of energies in space.

Now as to the value of the osmotic pressure in some liquids.

In 1000 cc. of water there are

$$\frac{1000}{18} = 55.55 \text{ gram-molecules.}$$

Every gram-molecule at 25° C. (= 298° absolute temperature) in 1000 cc. has a pressure of

$$\frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \text{ m.}$$

Hence for the 55.55 gram-molecules of water we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{18} = 1024 \text{ meters of mercury.}$$

In 1000 cc. methyl alcohol there are

$$\frac{1000}{32} \cdot 0.79 \text{ gram-molecules,}$$

and hence for methyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{32} \cdot 0.79 = 455 \text{ m.}$$

In 1000 cc. ethyl alcohol there are

$$\frac{1000}{46} \cdot 0.79 \text{ gram-molecules,}$$

and hence for ethyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{46} \cdot 0.79 = 316 \text{ m.}$$

In 1000 cc. propyl alcohol there are

$$\frac{1000}{60} \cdot 0.80 \text{ gram-molecules,}$$

and hence for propyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{46} \cdot 0.80 = 249 \text{ m.}$$

In 1000 cc. chloroform there are

$$\frac{1000}{119}.\ 1.52 \text{ gram-molecules,}$$

and hence for chloroform we have

$$\pi = \frac{22222}{1000}.\frac{298}{273}.\ 0.76\frac{1000}{119}.\ 1.52 = 235 \text{ m.}$$

In 1000 cc. toluene there are

$$\frac{1000}{92}.\ 0.88 \text{ gram-molecules,}$$

and hence for toluene we have

$$\pi = \frac{22222}{1000}.\frac{298}{273}.\ 0.76\frac{1000}{92}.\ 0.88 = 176 \text{ m.}$$

RUTGERS COLLEGE.

[CONTRIBUTIONS FROM THE LABORATORIES OF THE SCHOOL OF MINING, KINGSTON, ONTARIO.]

VOLUMETRIC ESTIMATION OF LEAD.

BY FRED. J. POPE.

Received May 21, 1896.

QUITE frequently of late, the attention of readers of chemical journals has been directed to various methods[1] for estimating lead volumetrically. But, while some of these methods are superior to any previously made public, yet, for none of them is that degree of accuracy claimed which is so essential in a reliable quantitative operation. The chief objection to all of these methods is the use of an outside indicator. However, by using an inside indicator and modifying slightly the usual preliminary steps (necessary for the conversion of the ore into the sulphate) results have been obtained by the writer which are quite satisfactory.

The operation may be briefly outlined as follows: The lead is first converted into lead sulphate, then into lead acetate. Excess of standard potassium bichromate is added, which precipitates the lead as lead chromate. The unused potassium bichromate is reduced by excess of standard arsenious acid, and this latter

[1] This Journal, 17, 901; *Engineering and Mining Journal*, July 7, 1894.

titrated with iodine solution, using starch paste as an indicator.

PREPARATION AND STANDARDIZING OF SOLUTIONS.

Taking tenth normal solution of iodine as the standard, 4.995 grams of arsenious acid per liter and 4.763 grams of potassium bichromate per liter give standard solutions of equivalent value per equal volumes.

Iodine.—12.7 grams are dissolved in concentrated potassium iodide solution and made up to one liter.

Arsenious Acid.—Dissolve 4.95 grams in twenty or thirty cc. of saturated, filtered solution of sodium carbonate, gently warming. If too strong heat is applied the arsenious acid cakes and dissolves with difficulty.

By means of a burette accurately measure ten to fifteen cc. of arsenious acid solution, running it into a large porcelain dish. Acidify faintly with sulphuric acid, add fifty cc. saturated solution of pure sodium bicarbonate, add starch paste and titrate with the iodine.

Potassium Bichromate.—Weigh out approximately five grams, dissolve and make up to one liter. Remove twenty-five cc. to a porcelain dish, add fifty cc. of the standard arsenious acid and proceed with titration as already indicated.

Note.—Since all commercial sodium bicarbonate will decolorize more or less iodine, it is well in neutralizing to get the neutral point exactly. When this is attained, add fifty cc. sodium bicarbonate and deduct its iodine value from the quantity consumed.

The Operation in Detail.—Take from three to seven grams of ore, according to its richness in lead. Place this in a deep three-inch porcelain dish, thoroughly moisten it with water, cover the dish with a watch-glass and for each gram of ore used add four to five cc. of a previously prepared mixture of two parts by volume of sulphuric acid, three parts by volume of nitric acid and one part by volume of water. When the reaction, which first results, diminishes, evaporate as nearly to dryness as is possible without spurting. Cool, fill the dish with cold water, stir well and allow to settle for two or three minutes. Filter and wash with cold water until most of the acid is removed. Convey the

filter paper with the precipitate to a 300 to 400 cc. beaker or Erlenmeyer flask and neutralize any remaining acid with dilute ammonia. To the porcelain dish add ten to fifteen cc. strong ammonium acetate, made decidedly acid with acetic acid. Add an equal volume of water and boil for two or three minutes, washing the sides of dish so as to remove any remaining lead sulphate. This solution is then added to the flask containing the precipitate and the whole boiled from seven to ten minutes with frequent stirring. Cool, neutralize with ammonia, add 100 cc. of standard potassium bichromate, stirring well. Filter into a half liter measuring flask, moistening the filter paper with dilute ammonia or ammonium acetate. Wash precipitate as much as is possible in the flask, using hot water. The filtrate make up to the mark, and for titrating remove 100 cc. to a large one and one-half liter porcelain basin. Add ten to twenty cc. (or less if ore is rich in lead) of standard arsenious acid. Make decidedly acid with forty per cent. sulphuric acid and stir until the yellow color disappears or the liquid has a greenish tinge. A large excess of sulphuric acid is to be avoided. Neutralize with saturated solution of sodium bicarbonate and then add an excess of fifty cc. If the solution has a deep greenish tinge dilute it with distilled water. Finally add starch paste and titrate with standard iodine solution.

As a test of the accuracy of method, five portions of pure lead sulphate were acted upon and the following results obtained:

Grams taken.	Grams found.
1.0	1.000568
1.1	1.099375
1.2	1.200467
1.3	1.300673
1.4	1.399571

With a specimen of galena containing quartz and calcium carbonate, the writer obtained the following percentages:

Grams taken.	Per cent. lead found.
0.7	81.89
0.7	81.96
0.71	81.94
0.68	81.90

As a test of the method in the hands of inexperienced operators, it was outlined and explained to four junior students, who with the galena ore already mentioned, obtained the following results:

Grams taken.	Per cent. lead found.
R. H = 0.7	81.86
G. E. R. = 0.7	81.78
S. D. { 1 = 0.7	82.00
S. D. { 2 = 0.85	81.89
G. E. S = 0.7	81.95

With another ore containing five per cent. of copper, twenty-six per cent. of iron, quartz and gypsum, one of the students obtained the following results:

Grams taken.	Per cent. lead found.
3.0	15.89
3.5	16.01
4.0	15.97

ESTIMATION OF SULPHIDES IN CALCIUM CARBIDE.

BY FRED. J. POPE.

Received May 21, 1896.

A WEIGHED quantity of calcium carbide was conveyed to a dry Erlenmeyer flask provided with a stop-cock funnel and a delivery tube, which latter led to a ten ounce wash bottle, this in turn being connected with a smaller one. The wash bottles contained 150 cc. lead acetate of known strength (about tenth normal). By means of a stop-cock water was carefully added until there was no further evolution of acetylene. On the reaction ceasing, twenty-five to forty cc. sulphuric acid (1:3) was run into the flask and the whole gently boiled, the liberated hydrogen sulphide passing into the wash bottles and precipitating the lead as lead sulphide. When the reaction had ceased the flask and liquid was washed free of hydrogen sulphide by a current of air and the contents of wash bottles filtered. The filtrate containing unconsumed lead acetate was made up to a half liter. To 100 cc. of this solution were added standard potassium bichromate, arsenious acid, etc., (as indicated in preceding article) and total amount of unconsumed lead acetate estimated. The difference between this

amount and the quantity of lead acetate started with gave amount precipitated by the hydrogen sulphide from which the sulphur existing as sulphide was calculated.

Grams calcium carbide taken.	Per cent. sulphur found.
2.4492	3.37
3.1234	3.57

No attempt was made to check the application of the method. It is obvious that the impure calcium carbide may have evolved other products capable of removing lead from the solution. It is the writer's intention to investigate this and other points connected with this method.

NOTE ON THE PRESENCE OF OIL IN BOILER SCALE.[1]

BY CHARLES A. DOREMUS.

Received June 9, 1896.

IT is difficult to remove cylinder oils, whether pure mineral or mixtures of mineral and animal from condensed exhaust steam. The practice of recovering steam either for the preparation of distilled water or for boiler feed water is now so general that opportunities for observing the troubles attending the procedure are not wanting.

This sample of water was obtained by melting the "core" of cakes of artificial ice. The sediment is fine, flocculent and of red color. When removed from the water and dried it is pulverulent. There is very slight evidence of oil in the dry mass, the moist sediment does not appear oily. The large proportion of oil extracted by ether shows how inefficient the filters were in purifying the condensed steam. Yet very great pains were taken at the ice plant to secure pure distilled water, and there was no visible oiliness in the water as it flowed to the freezing cans. Here however the corrosive action of the distilled water on the galvanized iron produced a mass of iron and zinc hydrates which in being pushed to the centre by the gradual formation of ice gathered the oil and carried it to the core.

Another specimen is one obtained from a steamboat trafficing on the Hudson river and using salt or brackish water in the surface condensers. The boilers were said to be foul with masses

[1] Read before the New York Section. June 5th, 1886.

of oil coating the sides and tubes. Having determined the presence of the salts of sea water in the boiler, due to leaky condensers, a treatment was suggested which caused a fine precipitate. This precipitate gathered the oil in masses easily brushed from the crown sheets. When this mass is treated with ether a dry powder remains and oil dissolves.

A third specimen sent for examination from a large plant in Chicago, evaporating 2500 gallons of filtered river water and 25,000 condenser water every twenty-four hours. Lubricating oil, mineral with ten per cent. animal, is freely used, and the fine clay in the water has together with some incrusting ingredients, caused the oil to form into balls.

The next two specimens are in striking contrast to the foregoing. This is light colored, one-quarter inch thick, has a layer of dense nature near what must have been the heated surface on which the scale formed while the bulk of the incrustation is fibrous. The incrustation consists of calcium carbonate and sulphate, with which is intermingled clay and organic matter, the latter partly oil.

The general appearance of the next sample is quite different. The incrustation is in thin sheets about three-sixteenths inch thick, of light slate color, and made up of alternating layers of deposit of varying hardness. The ingredients are again calcium carbonate and sulphate and clay, while there is much organic matter. This can be separated from the mineral in great part by a little acid. The presence of oil is then noticeable. The boiler of this plant is fed with Lake Michigan water and condenser water. The latter goes directly to the hot well of twenty barrels capacity. While there are no oil filters the boiler is provided with a skimmer, which draws off floating materials from just below the water line. The lubricating oil used is mineral with fifty per cent. animal.

Notwithstanding the skimmer, the scale has formed and baked into a hard mass. It is highly non-conducting. It can be held by the fingers quite near to where a portion is heated in a Bunsen flame, the heat of which distils out and ignites the oil. A few pieces of this scale heated in an improvised retort made from a test tube yield quite a gas flame. The presence of oil

to the extent of from twenty to fifty per cent. in the deposits and scale of marine boilers filled with fresh water, any loss being made up from the exhaust or from sea water has been fully set forth by Lewes,[1] who also gives the causes thereof and remedies therefor. He also alludes to the possibilities of this type of scale forming in stationary boilers.

The specimens presented serve to illustrate the importance of critically examining the nature of the "*organic matter*" of incrustations, the statement "loss of ignition" being far too general.

[CONTRIBUTED FROM THE LABORATORY OF THE LOUISIANA EXPERIMENT STATION AND SUGAR SCHOOL.]

OCCURRENCE OF THE AMINES IN THE JUICE OF SUGAR CANE.

BY J. L. BEESON.

Received June 15, 1896.

THE presence of amines in the products of the sugar beet has long been known, but until this sugar season they have not been known to exist in the juices of sugar cane. Last December, while working with the precipitate formed by the addition of lime water to cane juice, it was noticed that the product dried at about 110° C. had a fishy odor. Upon heating some of this in a test tube over a burner, an alkaline vapor was given off which had a fishy ammoniacal odor. So about 300 grams of the dried substance was gradually heated in a hard glass retort upon a sand bath until an almost complete destructive distillation was effected. The products evolved were passed through a condenser and then through a series of U tubes, each of which was kept at a temperature a little below the boiling-points of each of the principal amines. A solid collected in the condenser tube, and an illuminating gas escaped from the last U tube, which was kept at —10° C. These products were not examined. There collected in the first receptacle about twenty cc. of an acid liquid. This was made alkaline with caustic soda and distilled. The products as before were passed through the series of tubes maintained at the different temperatures, when there

[1] *Chem. News*, 63, 181.

collected in the first, along with some water, about five cc. of clear liquid, which was strongly alkaline, had a pungent fishy odor, combined with hydrochloric acid, and otherwise manifested the general properties of the amines. An attempt was made to further purify it by freeing it from the water, but the amount was too small to bring to a definite boiling-point. The remaining liquid was neutralized with hydrochloric acid, and slowly evaporated down, whereupon a few crystals, slightly colored and deliquescent, were obtained. The quantity was too small to admit of an elementary analysis, so it was not possible to say whether the product was a single amine or a mixture of amines. The filter cake, the refuse from the clarification of cane juice, gave the same odor and alkaline vapor upon heating. It was my aim to subject several pounds of the filter cake to the same treatment in order to fully clear up the question, if possible, but the amount of other work required of me prevented. The clearing up of the matter is of the greatest scientific and practical interest to the sugar industry, as it will doubtless throw light upon the nature both of the amido and albuminous bodies of the cane juice. I write the account of the work with the hope that some chemist may be induced to continue the work, as the writer will discontinue sugar work.

[CONTRIBUTED FROM THE LABORATORY OF THE LOUISIANA EXPERIMENT STATION AND SUGAR SCHOOL.]

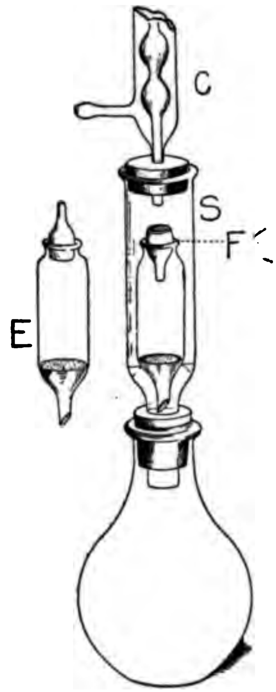
A SIMPLE AND CONVENIENT EXTRACTION APPARATUS FOR FOOD-STUFF ANALYSIS.

BY J. L. BEESON.

Received June 15, 1896.

THE apparatus shown in the accompanying illustration I have adapted from the Johnston extractor, for the general use of the average student in the laboratory aiming at simplicity, greater compactness, convenience, rapidity of operation, and accuracy. The extraction tube E, which is rather short, is provided as usual with a perforated platinum disk fused into the bottom, and in addition with a specially devised funnel stopper of ground glass, by means of which the weighed sample can be rapidly

and effectively dried to constant weight in a current of dry hydrogen or other inactive gas for the estimation of the moisture, and at the same time preparing the sample for extraction. Rubber caps are placed over the two ends of the tube during the cooling and weighing. For the extraction of the sample, the tube *E* is placed in a Stutzer tube *S* as shown in the figure, which is connected as usual with an ether flask below, and by means of either a cork or mercury joint with a short bulb condenser above. The funnel stopper, placed as shown, directs the returning drops of the liquid upon the center of the sample, and especially it prevents the loss of the sample by spattering. This is a source of objection to all forms of open extractors. Owing to the very small percentage of fats or ether extracts in most food stuffs a small loss of the sample from this cause makes a very large analytical error in the work, whether estimated from loss of the sample or gain in weight of the ether flask. During two years use in this laboratory we have obtained with the apparatus very concordant results between duplicate analyses, and would commend it for the use of students especially. By means of a seven mm. glass tube, six tubes and samples are dried in a current of hydrogen at a time in a water-oven. The whole apparatus may be had of Max Kaehler and Martini, Berlin.



NEW BOOKS.

CHEMISTRY FOR ENGINEERS AND MANUFACTURERS. BY BERTRAM BLOUNT AND A. G. BLOXAM. In two volumes. VOLUME I, CHEMISTRY OF ENGINEERING, BUILDING AND METALLURGY. 8vo. 244 pp. London: Charles Griffin & Co., Ltd. Philadelphia: J. B. Lippincott Co.

This work is a compilation of material intended to cover the chief branches of chemical industry. The first volume deals in

the first part with the chemistry of building materials, fuel, steam making and lubrication. The second part is entirely devoted to metallurgy.

The scope of the work necessitates condensation, yet the reader will be impressed at times with the meagerness of description, especially as the treatment of other subjects seems disproportionately extended. An appearance of unevenness in treatment is thus given, which might have been avoided.

Books of this class are more difficult to write as the limits of technical science are widened and there is room for much judgment in holding a proper balance between the necessities of the reader and the restricted space of a hand book or text book. While this book will be very serviceable to the large class of engineers and manufacturers for whom it is especially written, and even to the student of industrial chemistry, it can hardly be of much interest to " the expert in any one of the branches touched upon" (*vide* preface). The touch is entirely too light as a rule for those who seek extended information. The entire absence of references, also, deprives the work of much of the usefulness it might have had for professional readers in subjects not strictly their own.

The illustrations are good as far as they go, but are much less freely supplied than the nature of the book requires.

The subjects of gaseous fuel and water for steam making are well and clearly treated. Of boiler compositions the authors justly say that "none should be used without a knowledge both of its composition and of that of the water to be treated," and that, "all are sold at prices bearing but a remote relation to their intrinsic values." As to the preservation of iron by paint, the statement that red lead paint is the best will hardly meet unqualified assent.

The treatment of the metallurgy of iron is very full, and contains a good though brief discussion of the influence of foreign elements on the quality of iron. The statement that "the chief gold-producing countries are Australia, America (California), and Russia" is more compact than edifying. Electro-metallurgical processes are given in treating of many of the metals. The commercial production of aluminum is described

briefly but no allusion is made to the part which the United States have played in the development of this industry, nor do the names of Cowles or Hall appear in the text.

The second volume will treat of the chief chemical industries other than those referred to.

A. A. BRENEMAN.

LABORATORY EXPERIMENTS IN GENERAL CHEMISTRY. BY CHARLES R. SANGER, A.M., PH.D. Paper. St. Louis. Published by the Author. 1896.

EXPERIMENTS IN GENERAL CHEMISTRY AND QUALITATIVE ANALYSIS. BY CHARLES R. SANGER, A.M., PH.D. Paper. St. Louis. Published by the Author. 1896.

These two little books by Professor Sanger contain well selected collections of experiments for beginners in chemistry. The first collection was prepared for students in a general college course, while the second collection appears to have been arranged for students beginning a medical course. In the first collection for college students there is evidence that the author had in mind the needs of those who spend but part of a year in the laboratory. What the student is told to do is clearly indicated and his attention is directed at every step to the important points in the reactions considered. The experimental course offered to medical students is not as extended as the present writer would like to see, but is as full as this class of students is supposed to need, and has, besides, the advantage of systematic arrangement.

J. H. LONG.

BOOKS RECEIVED.

Eighth Annual Report of the Kentucky Agricultural Experiment Station of the State College of Kentucky, for the year 1895. Lexington, Ky. lxvi, 150 pp.

North Carolina Weather during the Year 1895. North Carolina Agricultural Experiment Station, Raleigh, N. C. lii, 264 pp.

Bulletin No. 122. Cost of Nitrogen, Phosphoric Acid and Potash. Proper Use of Tables of Analysis of Fertilizers. Connecticut Agricultural Experiment Station, New Haven, Conn. 16 pp.

Reduction of Nitrates by Bacteria and Consequent Loss of Nitrogen. By Ellen H. Richards and George William Rolfe. 20 pp. Reprinted from the *Technology Quarterly*, Vol. IX, No. 1, March, 1896.

Nitro-Explosives. A Practical Treatise. By P. Gerald Sanford, F. I. C.,

F. C. S. London: Crosby, Lockwood & Son. 1896. xii, 270 pp. Price, 9s.

Embalming and Embalming Fluids, with the Bibliography of Embalming. Thesis by Charles W. McCurdy, Sc.D., Ph.D. Wooster, Ohio: The Herald Publishing Co. April, 1896. 84 pp.

Bulletin No. 64. Analysis of Commercial Fertilizers. Kentucky Agricultural Experiment Station of the State of Kentucky, Lexington, Ky. July, 1896. 16 pp.

OBITUARY NOTE.

PETER COLLIER, Ph.D., was born in Chittenango, New York, August 17, 1835. He graduated A.B. at Yale College in 1861 and later Ph.D. He also graduated at the Sheffield Scientific School, and was for some time an assistant and instructor in that School. From 1867 to 1877, he was Professor of Physics and Chemistry in the University of Vermont, and also Professor of Chemistry in the Medical Department of that University, and for some time Dean of the Medical Faculty. In 1873 he was appointed one of seven scientific commissioners to the Vienna Exposition, by President Grant. From 1877 to 1882 he was Chief Chemist to the Department of Agriculture of the United States, at Washington. During his official term, he gave very great attention to the problems of cultivating sorghum and manufacturing sugar from it. From 1882 to 1885 he still remained in Washington, engaged in chemical pursuits and writing for scientific and agricultural publications. From 1887 to 1895 he was Director of the New York State Experiment Station at Geneva, New York, where he instituted much experimental work especially upon fertilizers and dairy problems. He had a wide acquaintance with scientific men, and himself possessed great energy and force. Illness obliged him to resign his position last year and he came to Ann Arbor last December. He died on June 29.

A. B. PRESCOTT.

ERRATA.

On page 651, July number, 15th line from top, for 159,000 *read* 166,000.
On page 653, 7th line from bottom, for 159,000 *read* 166,000.
On page 654, 4th line from top, for 136,519.5 *read* 116,519.5.

VOL. XVIII. [SEPTEMBER, 1896.] NO. 9.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE DETERMINATION OF REDUCING SUGARS IN TERMS OF CUPRIC OXIDE.

BY GEORGE DEFREN.

Received July 9, 1896.

IT is now approximately fifty years since alkaline metallic solutions were first used in determining quantitatively the various reducing sugars. During this period of time many investigators have worked on the subject, and much has been done towards perfecting the method of analysis, so that to-day there are several admirable processes in use for the exact estimation of these carbohydrates.

The quantitative methods of determining reducing sugars may be divided into two main classes: those based upon the volumetric plan, and those which depend on a gravimetric estimation of the precipitated cuprous oxide.

Of the first class many processes have been suggested which have met with more or less success. The volumetric methods are mainly used for factory control work, where the progress of some processes require a rapid and fairly accurate idea of the stage of manufacture. In expert hands the volumetric methods are capable of giving excellent and concordant results, and are, therefore, used in the laboratories of many consulting chemists, and even in scientific institutions.

The main objections to the use of the volumetric methods are that each freshly prepared quantity of Fehling solution requires accurate standardization against the same kind of pure sugar as that which is undergoing analysis. Different dilutions and the

time of boiling affect the results materially. The exact determination of the "end point" also requires considerable practice and skill.

On the other hand, the Fehling liquor used in the gravimetric processes need not be made up as accurately as is required for volumetric work. The gravimetric methods, however, ordinarily require more time. A possible loss of cuprous oxide by filtration, and an incomplete oxidation to the higher oxide are also potent factors, though where the requisite degree of care is exercised these need not cause anxiety. The same statement regarding dilution and time of boiling holds true with as much force in gravimetric as in volumetric work.

The gravimetric methods are generally employed for scientific and accurate analytical work. Here the processes are comparatively few, all depending upon the oxidation of the total sugar present in an excess of the alkaline copper solution.

The tables in use for the determination of reducing sugars are mainly constructed in terms of metallic copper. As the amount of metal precipitated per gram of carbohydrate is not a constant for all dilutions of any sugar, specially constructed tables are generally employed. Several such tables have been prepared, as for instance Allihn's table of reduced copper for dextrose, Wein's table for maltose, and Soxhlet's table for lactose, etc.

Various modifications of the alkaline copper solutions are used for the determination of the different sugars, each requiring special treatment. Therefore a chemist in determining the amount of malt sugar in, say beer, must, if he uses Wein's table for maltose, follow exactly Wein's method for the estimation of that sugar.

Where a variety of work is carried on in a laboratory, it is therefore necessary to have several different Fehling solutions on hand for each special kind of determination. If all the tables for the estimation of the different carbohydrates could have been prepared for use under uniform conditions, the existing state of affairs would be much simplified.

In order to supply this need, I have constructed such tables, using a method which I have employed for some time, in deter-

mining reducing sugars. This method, proposed by O'Sullivan[1] in 1876, is used to some extent in England, but as it seems to be not generally known, I here give the procedure in detail:

To fifteen cc. of the copper sulphate solution, prepared as given below, are added fifteen cc. of the alkaline tartrate solution, in an Erlenmeyer flask having a capacity of from 250–300 cc. The mixture is diluted with fifty cc. of freshly boiled distilled water and placed in a boiling water bath for five minutes. Twenty to twenty-five cc. accurately measured from a calibrated burette of an approximately one-half per cent. solution of the sugar to be analyzed, are then run into the hot Fehling liquor and the whole kept in the boiling water bath for from twelve to fifteen minutes. The flask is then removed from the bath and the precipitated cuprous oxide is filtered as rapidly as possible, either through filter paper or asbestos in a Soxhlet's tube or porcelain Gooch crucible, and washed with boiling distilled water until the wash water no longer reacts alkaline. It is ignited and weighed as cupric oxide as described below. The corresponding amounts of dextrose, maltose or lactose are ascertained by reference to the tables at the end of this article. It should be noted that the above directions must be closely followed. The volume of the Fehling liquor and the added sugar solution should be from 100–105 cc.

The Fehling solution used is made up according to Soxhlet's formula, with a very slight modification. 69.278 grams of pure crystallized copper sulphate, pulverized and dried between filter paper, are dissolved in distilled water. It is advantageous to add one cc. of strong sulphuric acid to this, as recommended by Sutton.[2] The whole is then made up to one liter with distilled water and kept in a separate bottle. The alkaline tartrate solution is made by dissolving 356 grams of crystalline Rochelle salt and 100 grams of sodium hydroxide in distilled water and making up to one liter. This is also kept in a separate bottle.

Two methods of filtration of the precipitated cuprous oxide and further treatment are generally adopted. In the first double "washed" filter paper is used; in the other the precipitate is

[1] *J. Chem. Soc.*, 2, 130, *1876*.
[2] Sutton: Fourth edition, (1882), 256.

retained by a layer of asbestos. After washing the precipitate on the filter paper as above described, it is dried in the usual manner and ignited in a previously weighed porcelain crucible, taking care to burn the filter paper cautiously, heating for fifteen minutes to a red heat, cooling the crucible over sulphuric acid in a desiccator and weighing as cupric oxide. Additional treatment with nitric acid has been found of no practical advantage, the results by direct ignition being very exact, providing the filter paper is slowly burned. The chief objection to the employment of filter paper to retain the precipitated cuprous oxide, is that some of the finely divided particles are liable to go through, thus causing low results.

As a substitute for paper carefully selected asbestos is often used for filtering purposes. To insure a layer of asbestos which shall be kept at constant weight under the action of hot Fehling liquor, it is advantageous to boil the mineral with nitric acid (1.05–1.10 sp. gr.) for a short time, washing the acid out with hot water, and then boiling with a twenty-five per cent. solution of sodium hydroxide. This is also washed out with hot water. Reboiling with the above reagents as before diminishes the liability of leaving any soluble portions. As thus prepared the filtering material may be kept indefinitely under water in a wide-mouthed bottle ready for use.

The objections of some chemists[1] to the employment of asbestos on the ground that it loses weight on using, does not seem to hold, when it is prepared as above. A sample boiled as stated with acid and alkali three times, lost only two-tenths milligram when two "blanks" of hot dilute Fehling solution, as used in the process above described, were passed through the mineral in a porcelain Gooch crucible.

For use, a layer of asbestos, about one centimeter in thickness, is placed in a porcelain Gooch crucible, to retain the finely divided precipitate, which is filtered by means of suction, in the usual manner. The crucible containing the cuprous oxide is then dropped into a triangular frame, made of platinum wire, suspended within an iron radiator, or shell, heated to redness. This quickly and thoroughly dries the asbestos without cracking

[1] Killing: *Ztschr. angew. Chem.*, 431, *1894*; Praeger: *Ztschr. angew. Chem.*, 520, *1894*.

the crucible. After about five minutes the crucible is transferred by means of a pair of nippers to a red hot platinum crucible and heated for about fifteen minutes. It is then quickly transferred to a desiccator near at hand to prevent cracking, allowed to cool and weighed. As cupric oxide is somewhat hygroscopic, it is advantageous to weigh quickly and to keep the balance case as dry as possible. Prolonged heating in the iron radiator would have changed the cuprous oxide to the cupric state. The advantage of transferring the porcelain crucible to a red-hot platinum crucible, is that the oxidation is quickly completed, as a much higher temperature is available.

If pressed for time, another determination can be made in the same crucible without cleaning it. As a rule, it is, however, advisable to wash out the cupric oxide by means of hot nitric acid (1.05–1.10 sp. gr.) and then with hot water. The crucible is then heated, cooled and weighed as before. It must necessarily be weighed, because this treatment with hot nitric acid dissolves some of the asbestos.

If preferred, a Soxhlet's tube may be used to retain the precipitated cuprous oxide. As a porcelain Gooch crucible possessed obvious advantages over this apparatus, I have used it in all my determinations with success.

The cupric reducing powers of dextrose, maltose aud lactose were determined by the method given above. A table for invert sugar was not constructed because most invert sugar determinations are made by double polarization in a saccharimeter.

DEXTROSE.

The "cupric reducing power" of dextrose was first determined. This is defined as "the amount of cupric oxide which 100 parts reduce."[1] This may be represented by $\frac{100\ W}{D}$, in which W is the weight of cupric oxide obtained by the given weight of any sugar, and D the weight of cupric oxide formed by an equal weight of dextrose.[2] Hence, if the amount of cupric oxide formed by one gram of dextrose be known, the amount of cupric oxide reduced by one gram of any other substance, calculated

[1] *J. Chem. Soc.*, 2, 130, *1876*.
[2] *J. Chem. Soc.*, *Trans.*, 606, *1879*.

upon this number as a percentage, will represent the cupric oxide reducing power of the substance, which we denote by the symbol K.

The amount of cupric oxide has been determined by O'Sullivan[1] to be 2.205 grams per gram dextrose. The factor for dextrose in terms of cupric oxide is, therefore, the reciprocal of 2.205 or 0.4535. This value, 0.4535, was assumed to be a constant for all amounts of dextrose when used with Fehling's solution in the manner indicated. As such it was a very convenient quantity, it being only necessary to obtain the weight of cupric oxide formed by the action of a dextrose solution, multiply this by 0.4535, and the amount of dextrose corresponding was obtained. No tables are needed if this assumption be true. Consequently the determination of dextrose was indeed a very simple one.

On an extended investigation of this subject, using various amounts of dextrose on the same volume of Fehling liquor in each determination, I find that the value 2.205, above given as representing the quantity of cupric oxide obtained by the action of one gram of dextrose, is not as was heretofore assumed, a constant for all weights of dextrose taken, the amount varying from 2.27 grams cupric oxide per gram dextrose for small quantities of sugar, to 2.22 grams cupric oxide for the largest amount of dextrose permissible. Allihn,[2] boiling his sugar solutions with the Fehling liquor and reducing the cuprous oxide to copper, obtained analogous varying results.

The purity of the dextrose used was first determined, dextrose anhydride being employed. 10.008 grams of anhydrous dextrose were disssolved in distilled water and the solution boiled to prevent birotation. It was then transferred to a flask, the capacity of which at 15.5° C. was 100.08 cc., thus giving a solution which contained 0.100 gram dextrose anhydride per cc.

The specific gravity of the above solution at 15.5° was determined in the usual manner by means of a picnometer with thermometer attached.

Capacity picnometer (at 15.5°) = 55.2055 cc.
Dextrose solution (at 15.5°) = 57.3083 grams.

[1] *Loc. cit.*

[2] *J. prakt. Chem.*, (2), 22, 63.

On calculating from these values we find the specific gravity of a dextrose solution containing ten grams dextrose in 100 cc. to be 1.03809 at 15.5°.

The specific rotatory power was determined by the usual method, a Schmidt and Haensch saccharimeter being used in polarizing the dextrose solution. The polarizations were carried out in a 200 millimeter tube at 20°. To change from the readings of a saccharimeter to the rotary degrees, it is necessary to multiply the reading observed by 0.344, as shown by Reinbach.[1] I have verified this value with concordant results, a Laurent polariscope being used for comparison. The rotation of the above solution was 30.7 divisions. This gives by means of the usual formula — $[\alpha]_D^{20} = \frac{\alpha v}{lw}$ —a specific rotatory power of 52.8°, which is in accordance with that obtained by other observers.[2] The dextrose used was consequently pure.

For the determination with Fehling liquor, twenty-five cc. of the dextrose solution at 15.5° were accurately measured from a calibrated burette and made up to 500 cc. with distilled water at the same temperature. This consequently gave a solution, each cubic centimeter of which contained five milligrams dextrose. Various quantities of this were then taken to ascertain the cupric reducing power of dextrose. The results in detail are given below. In each case the combined volumes of the Fehling liquor and the sugar solution were made up to 105 cc. as described above.

Milligrams dextrose.	Cupric oxide obtained.	Cupric oxide per gram dextrose.	Dextrose equivalent.	Mean dextrose equivalent.
12½	0.0283	2.264	0.4416	0.4401
12½	0.0285	2.280	0.4386	
25	0.0569	2.276	0.4393	0.4419
25	0.0565	2.260	0.4425	
50	0.1129	2.258	0.4429	0.4440
50	0.1123	2.246	0.4452	
62½	0.1407	2.251	0.4443	0.4449
62½	0.1403	2.245	0.4454	
75	0.1683	2.244	0.4457	0.4462
75	0.1679	2.239	0.4467	

1 *Ber. d. chem. Ges.*, 27, 2282.

2 Pribram : *Monat. f. Chem.*, 9, 399; Landolt : *Ber. d. chem. Ges.*, 21, 191.

Milligrams dextrose.	Cupric oxide obtained.	Cupric oxide per gram dextrose.	Dextrose equivalent.	Mean dextrose equivalent.
100	0.2233	2.233	0.4478	0.4483
100	0.2227	2.227	0.4489	
125	0.2776	2.221	0.4503	
125	0.2782	2.225	0.4493	
125	0.2770	2.216	0.4512	0.4503
125	0.2774	2.219	0.4506	
125	0.2777	2.222	0.4500	
140	0.3105	2.218	0.4508	0.4511
140	0.3100	2.215	0.4515	

The foregoing values of the amounts of cupric oxide per gram dextrose are given graphically in curve *A*, Plot I, and the dextrose equivalents of this in *A*, Plot II.

From this we get the amount of dextrose corresponding to a given weight of copper oxide by means of the formula:

$$D = (0.4400 + 0.000037\ W)\ W,$$

in which D is the amount of dextrose, and W the weight of cupric oxide.

The dextrose table given in this article is based on this formula, the values of W varying from 30 to 320.

MALTOSE.

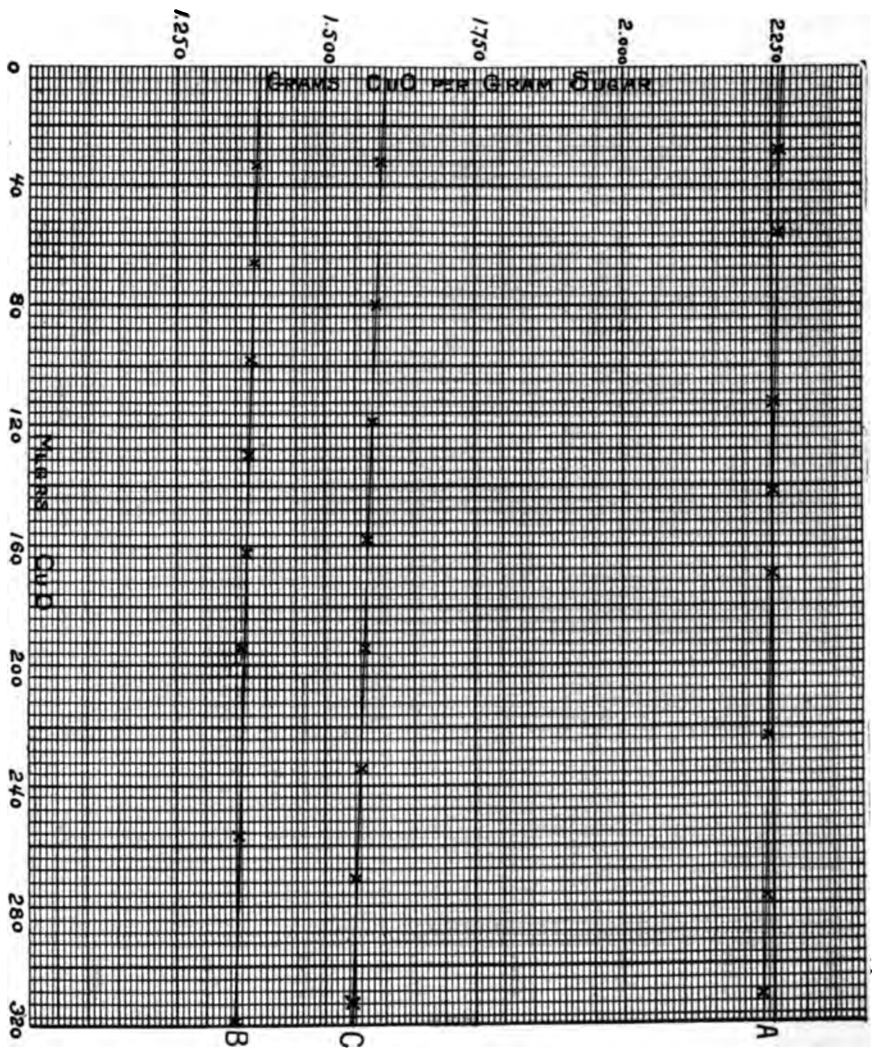
The cupric reducing power of dextrose is given as 100. Using this as a basis, the reducing force of maltose, as given by O'Sullivan,[1] is 65. Brown and Heron[2] place the value somewhat lower, claiming that 61 is more exact. The results which I have obtained agree very well with this latter number.

In the case of maltose, as with dextrose, it was found that the amount of cupric oxide obtained per gram of sugar was not a constant. The cupric reducing power of various amounts of maltose was, however, found to be almost exactly a constant when referred to the cupric oxide from equal weights of dextrose. That is, calling the reducing power of dextrose 100 for different aliquot parts of that sugar, the cupric reducing power of maltose referred to this standard was always 61.

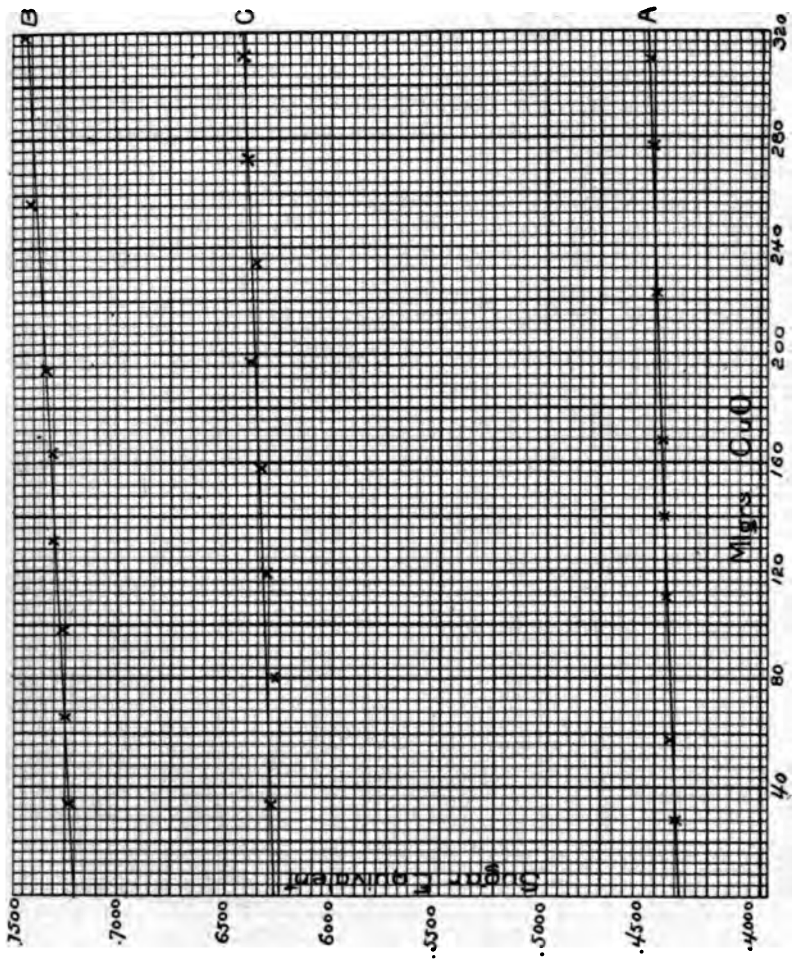
The specific gravity of maltose was determined in the usual manner. 9.7558 grams maltose anhydride were dissolved in distilled water to 100.08 cc. at 15.5°.

[1] *Loc. cit.*

[2] *J. Chem. Soc.*, *1879*, Trans., 619.


Grams CuO per Gram Sugar
Mlgrs CuO
1.250
1.500
1.750
2.000
2.250
0
40
80
120
160
200
240
280
320
B
C
A

Plot 1.


B
C
A
Sugar Equivalent
Mlgrs CuO
40
80
120
160
200
240
280
320
.7500
.7000
.6500
.6000
.5500
.5000
.4500
.4000

Plot 2.

Maltose solution at 15.5° = 57.3049 grams.

On calculating this we find the specific gravity of the above solution to be 1.03803. For a solution containing ten grams maltose anhydride in 100 cc. it would consequently be 1.03900 at 15.5°.

The specific rotatory power was determined as usual. The rotation of the above solution at 20°, in a 200 millimeter tube, was 74.4 divisions on the saccharimeter scale. This gives $[\alpha]_D^{20} =$ 136.6°.

As maltose anhydride is somewhat difficult to prepare, the solutions used to determine the cupric reducing powers were made up to approximately ten per cent. from the maltose hydrate. The specific gravity of the solutions was then determined. Subtracting from this value 1.00000—the specific gravity of water—and dividing the remainder by 0.00390, we get the amount of maltose anhydride in 100 cc. of solution.

Maltose solution at 15.5° = 57.2511 grams,

which gives a specific gravity of 1.03754, or 9.501 grams maltose anhydride in 100 cc.

The solution for Fehling determinations was made in the same manner as the dextrose solutions above. Each cubic centimeter of the diluted maltose solution therefore contained 4.75 milligrams maltose anhydride.

Milligrams maltose.	Cupric oxide obtained.	Cupric oxide per gram maltose.	Maltose equivalent.	Mean maltose equivalent.
23.75	0.0329	1.386	0.7218	0.7240
23.75	0.0327	1.377	0.7263	
47.5	0.0656	1.381	0.7243	0.7253
47.5	0.0654	1.377	0.7263	
71.25	0.0983	1.380	0.7247	0.7263
71.25	0.0979	1.374	0.7278	
95.0	0.1304	1.373	0.7286	0.7297
95.0	0.1300	1.369	0.7308	
118.75	0.1623	1.370	0.7302	0.7319
118.75	0.1619	1.367	0.7336	
142.5	0.1940	1.361	0.7345	0.7354
142.5	0.1934	1.357	0.7369	
190.0	0.2572	1.353	0.7284	0.7395
190.0	0.2566	1.350	0.7406	
237.5	0.3198	1.347	0.7429	0.7433
237.5	0.3193	1.345	0.7437	

The maltose equivalent in terms of copper oxide is shown in *B*, Plot II. From this we get the amount of maltose corresponding to a given weight of cupric oxide by the formula:

$$M = (0.7215 + 0.000061\ W)\,W,$$

in which M is the weight of maltose, and W the amount of cupric oxide obtained. It will be seen that these values make the cupric reducing power of maltose 0.61 that of dextrose.

LACTOSE.

Lactose was investigated in the same manner as the preceding. 10.008 grams lactose anhydride were dissolved in distilled water, boiled, and made up to 100.08 cc. at 15.5°.

The above solution, polarized in a 200 millimeter tube at 20°, gave a rotation of 30.7 divisions. This gives the specific rotary power of lactose of 52.8°.

The amounts of cupric oxide found by the reduction of known weights of lactose were determined as in the previous cases with the following results:

Milligrams lactose.	Cupric oxide obtained.	Cupric oxide per gram lactose.	Lactose equivalents.	Mean lactose equivalents.
20	0.0319	1.595	0.6269	0.6289
20	0.0317	1.585	0.6308	
50	0.0798	1.596	0.6266	0.6274
50	0.0796	1.592	0.6282	
75	0.1188	1.584	0.6313	0.6323
75	0.1184	1.579	0.6334	
100	0.1577	1.577	0.6340	0.6355
100	0.1570	1.570	0.6369	
125	0.1955	1.564	0.6395	0.6379
125	0.1964	1.561	0.6363	
150	0.2345	1.563	0.6397	0.6404
150	0.2340	1.560	0.6410	
175	0.2729	1.560	0.6412	0.6418
175	0.2724	1.557	0.6424	
200	0.3112	1.556	0.6425	0.6430
200	0.3107	1.553	0.6436	

The cupric oxide values per gram lactose are presented graphically in curve *C*, Plot I, while the reciprocals of these quantities are shown in *C*, Plot II. For this latter the amount of lactose corresponding to the weight of cupric oxide obtained is determined by the following:

$$L = (0.6270 + 0.000053\ W)\ W,$$

in which L is the lactose, and W the amount of copper oxide. The acompanying table for lactose is constructed on this basis.

* * * * * * *

It will be seen from the above results that the amount of cupric oxide produced by the action of one gram of reducing carbohydrate on Fehling liquor, in the manner described, is not a constant for all dilutions.

The cupric reducing power of maltose is 0.61 that of dextrose.

The following tables for the determination of the reducing sugars in terms of cupric oxide are based on the analytical results presented above, and can be used in the process outlined in the same manner as any other table for the same purpose:

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
30	13.2	21.7	18.8	57	25.1	41.3	35.9
31	13.7	22.4	19.5	58	25.5	42.1	36.5
32	14.1	23.1	20.1	59	26.0	42.8	37.1
33	14.6	23.9	20.7	60	26.4	43.5	37.8
34	15.0	24.6	21.4	61	26.9	44.3	38.4
35	15.4	25.3	22.0	62	27.3	45.0	39.0
36	15.9	26.1	22.6	63	27.8	45.7	39.7
37	16.3	26.8	23.3	64	28.2	46.5	40.3
38	16.8	27.5	23.9	65	28.7	47.2	40.9
39	17.2	28.3	24.5	66	29.1	47.9	41.6
40	17.6	29.0	25.2	67	29.5	48.6	42.2
41	18.1	29.7	25.8	68	30.0	49.4	42.8
42	18.5	30.5	26.4	69	30.4	50.1	43.5
43	19.0	31.2	27.1	70	30.9	50.8	44.1
44	19.4	31.9	27.7	71	31.3	51.6	44.7
45	19.9	32.7	28.3	72	31.8	52.3	45.4
46	20.3	33.4	29.0	73	32.2	53.0	46.0
47	20.7	34.1	29.6	74	32.6	53.8	46.6
48	21.2	34.8	30.2	75	33.1	54.5	47.3
49	21.6	35.5	30.8	76	33.5	55.2	47.9
50	22.1	36.2	31.5	77	34.0	56.0	48.5
51	22.5	37.0	32.1	78	34.4	56.7	49.2
52	23.0	37.7	32.7	79	34.9	57.4	49.8
53	23.4	38.4	33.3	80	35.4	58.1	50.5
54	23.8	39.2	34.0	81	35.9	58.9	51.1
55	24.2	39.9	34.6	82	36.3	59.6	51.7
56	24.7	40.5	35.2	83	36.8	60.3	52.4

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
84	37.2	61.1	53.0	127	56.5	92.5	80.4
85	37.7	61.8	53.6	128	56.9	93.3	81.1
86	38.1	62.5	54.3	129	57.3	94.0	81.7
87	38.5	63.3	54.9	130	57.8	94.8	82.4
88	39.0	64.0	55.5	131	58.2	95.5	83.0
89	39.4	64.7	56.2	132	58.7	96.2	83.6
90	39.9	65.5	56.8	133	59.1	97.0	84.2
91	40.3	66.2	57.4	134	59.6	97.7	84.9
92	40.8	66.9	58.1	135	60.0	98.4	85.5
93	41.2	67.7	58.7	136	60.5	99.2	86.1
94	41.7	68.4	59.3	137	60.9	99.9	86.8
95	42.1	69.1	60.0	138	61.3	100.7	87.4
96	42.5	69.9	60 6	139	61.8	101.4	88.1
97	43.0	70.6	61.2	140	62.2	102.1	88.7
98	43.4	71.3	61.9	141	62.7	102.8	89.3
99	43.9	72.1	62.5	142	63.1	103.5	90.0
100	44.4	72.8	63.2	143	63.6	104.3	90.6
101	44.8	73.5	63.8	144	64.0	105.0	91.3
102	45.3	74.3	64.4	145	64.5	105.8	91.9
103	45.7	75.0	65.1	146	64.9	106.5	92.6
104	46.2	75.7	65.7	147	65.4	107.2	93.2
105	46.6	76.5	66.3	148	65.8	108.0	93.9
106	47.0	77.2	67.0	149	66.3	108.7	94.5
107	47.5	77.9	67.6	150	66.8	109.5	95.2
108	48.0	78.7	68.2	151	67.3	110.2	95.8
109	48.4	79.4	68.9	152	67.7	111.0	96.5
110	48.9	80.1	69.5	153	68.3	111.7	97.1
111	49.3	80.9	70.1	154	68.7	112.4	97.8
112	49.8	81.6	70.8	155	69.2	113.2	98.4
113	50.2	82.3	71.4	156	69.6	113.9	99.1
114	50.7	83.1	72.0	157	70.0	114.7	99.7
115	51.1	83.8	72.7	158	70.5	115.4	100.4
116	51.6	84.5	73.3	159	70.9	116.1	101.0
117	52.0	85.2	74.0	160	71.3	116.9	101.7
118	52.4	85.9	74.6	161	71.8	117.6	102.3
119	52.9	86.6	75.2	162	72.3	118.4	103.0
120	53.3	87.4	75.9	163	72.7	119.1	103.6
121	53.8	88.1	76.6	164	73.2	119.9	104.3
122	54.2	88.9	77.2	165	73.6	120.6	104.9
123	54.7	89.6	77.9	166	74.1	121.4	105.6
124	55.1	90.3	78.5	167	74.5	122.1	106.2
125	55.6	91.1	79.1	168	74.9	122.9	106.9
126	56.0	91.8	79.8	169	75.4	123.6	107.5

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
170	75.8	124.4	108.2	213	95.3	156.3	136.0
171	76.3	125.1	108.8	214	95.8	157.1	136.7
172	76.8	125.8	109.5	215	96.3	157.8	137.3
173	77.3	126.6	110.1	216	96.7	158.6	138.0
174	77.7	127.3	110.8	217	97.2	159.3	138.6
175	78.2	128.1	111.4	218	97.6	160.0	139.3
176	78.6	128.8	112.0	219	98.1	160.8	139.9
177	79.1	129.5	112.6	220	98.6	161.5	140.6
178	79.5	130.3	113.3	221	99.0	162.3	141.2
179	80.0	131.0	113.9	222	99.5	163.0	141.9
180	80.4	131.8	114.6	223	99.9	163.7	142.5
181	80.8	132.5	115.2	224	100.4	164.5	143.2
182	81.3	133.2	115.8	225	100.9	165.3	143.8
183	81.8	134.0	116.5	226	101.3	166.0	144.5
184	82.2	134.7	117.1	227	101.8	166.8	145.1
185	82.7	135.5	117.8	228	102.2	167.5	145.8
186	83.1	136.2	118.4	229	102.7	168.3	146.4
187	83.5	136.9	119.1	230	103.1	169.1	147.0
188	84.0	137.7	119.7	231	103.6	169.8	147.7
189	84.4	138.4	120.4	232	104.0	170.6	148.3
190	84.9	139.1	121.0	233	104.5	171.3	149.0
191	85.4	139.9	121.7	234	105.0	172.1	149.6
192	85.9	140.6	122.3	235	105.4	172.8	150.3
193	86.3	141.4	123.0	236	105.9	173.6	150.9
194	86.8	142.1	123.6	237	106.3	174.3	151.6
195	87.2	142.8	124.3	238	106.8	175.1	152.2
196	87.7	143.6	124.9	239	107.2	175.8	152.9
197	88.1	144.3	125.6	240	107.7	176.6	153.5
198	88.6	145.1	126.2	241	108.1	177.3	154.2
199	89.0	145.8	126.9	242	108.6	178.1	154.8
200	89.5	146.6	127.5	243	109.0	178.8	155.5
201	89.9	147.3	128.2	244	109.5	179.6	156.1
202	90.4	148.1	128.8	245	109.9	180.3	156.8
203	90.8	148.8	129.5	246	110.4	181.1	157.4
204	91.3	149.6	130.1	247	110.9	181.8	158.1
205	91.7	150.3	130.8	248	111.3	182.6	158.7
206	92.2	151.1	131.5	249	111.8	183.3	159.4
207	92.6	151.8	132.1	250	112.3	184.1	160.0
208	93.1	152.5	132.8	251	112.7	184.8	160.7
209	93.5	153.3	133.4	252	113.2	185.5	161.3
210	94.0	154.1	134.1	253	113.7	186.3	162.0
211	94.4	154.8	134.7	254	114.1	187.1	162.6
212	94.9	155.6	135.4	255	114.6	187.8	163.3

Parts. copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts. copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose
256	115.0	188.6	163.9	289	130.2	213.6	185.6
257	115.5	189.3	164.6	290	130.6	214.3	186.2
258	116.0	190.1	165.2	291	131.1	215.1	186.9
259	116.4	190.8	165.9	292	131.5	215.9	187.6
260	116.9	191.6	166.5	293	132.0	216.6	188.2
261	117.3	192.4	167.2	294	132.5	217.4	188.9
262	117.8	193.1	167.8	295	133.0	218.2	189.5
263	118.3	193.9	168.5	296	133.4	218.9	190.2
264	118.7	194.6	169.1	297	133.9	219.7	190.8
265	119.2	195.4	169.8	298	134.3	220.4	191.5
266	119.6	196.1	170.4	299	134.8	221.2	192.1
267	120.1	196.9	171.1	300	135.3	221.9	192.8
268	120.6	197.7	171.7	301	135.7	222.7	193.4
269	121.0	198.4	172.4	302	136.2	223.5	194.1
270	121.4	199.2	173.0	303	136.6	224.2	194.7
271	121.9	199.9	173.7	304	137.1	225.0	195.3
272	122.4	200.7	174.4	305	137.6	225.8	196.0
273	122.8	201.5	175.0	306	138.0	226.5	196.6
274	123.3	202.2	175.7	307	138.5	227.3	197.3
275	123.7	203.0	176.3	308	138.9	228.1	197.9
276	124.2	203.7	177.0	309	139.4	228.8	198.6
277	124.6	204.5	177.6	310	139.9	229.6	199.3
278	125.1	205.2	178.3	311	140.3	230.4	199.9
279	125.6	206.0	178.9	312	140.8	231.1	200.6
280	126.1	206.8	179.6	313	141.2	231.9	201.3
281	126.5	207.5	180.2	314	141.7	232.7	202.0
282	127.0	208.3	180.9	315	142.2	233.4	202.6
283	127.4	209.0	181.5	316	142.6	234.2	203.3
284	127.9	209.8	182.2	317	143.1	234.9	203.9
285	128.3	210.5	182.9	318	143.6	235.7	204.6
286	128.8	211.3	183.6	319	144.0	236.5	205.3
287	129.3	212.1	184.2	320	144.5	237.2	205.9
288	129.7	212.8	184.9				

SUPPLEMENTARY TABLE FOR GLUCOSE ANALYSIS.

The amounts of cupric oxide given above are those obtained by the use of absolute weights of sugar. The tables are constructed on this basis. In the case of a mixed product, like commercial glucose, which may be considered made up of the simple bodies, dextrin, maltose, and dextrose, it is far more convenient to determine the total carbohydrates present in solution by means of the specific gravity than by drying the glucose and

obtaining in this way the total solids. For this purpose an arbitrary value is taken which shall represent the influence of one gram of a mixture of the three substances above mentioned on the specific gravity if dissolved to 100 cc. in distilled water. Brown and Heron[1] claim that this influence on the specific gravity of one gram starch conversion product in 100 cc. is 0.00386. This value has been determined to be correct for solutions of cane sugar, and is much used for glucose work.

As above mentioned the specific gravity of a dextrose solution containing ten grams dextrose anhydride in 100 cc. is 1.03809 at 15.5°. To determine the cupric reducing power of a substance using the value 3.86 as a divisor, it therefore becomes necessary to change the figures given in the tables to conform to this new factor, that is, the dextrose equivalents must be multiplied by $\frac{386}{381}$, which has been done for convenience of reference in the following table:

Copper oxide obtained.	Dextrose equivalent.	Copper oxide obtained.	Dextrose equivalent.	Copper oxide obtained.	Dextrose equivalent.
5	0.4461	110	0.4500	215	0.4540
10	0.4463	115	0.4502	220	0.4542
15	0.4465	120	0.4504	225	0.4543
20	0.4467	125	0.4506	230	0.4545
25	0.4468	130	0.4508	235	0.4547
30	0.4470	135	0.4510	240	0.4549
35	0.4472	140	0.4512	245	0.4551
40	0.4474	145	0.4513	250	0.4553
45	0.4476	150	0.4515	255	0.4555
50	0.4478	155	0.4517	260	0.4557
55	0.4480	160	0.4519	265	0.4558
60	0.4482	165	0.4521	270	0.4560
65	0.4484	170	0.4523	275	0.4562
70	0.4485	175	0.4525	280	0.4564
75	0.4487	180	0.4527	285	0.4566
80	0.4489	185	0.4528	290	0.4568
85	0.4491	190	0.4530	295	0.4570
90	0.4493	195	0.4532	300	0.4572
95	0.4495	200	0.4534	305	0.4574
100	0.4497	205	0.4536	310	0.4576
105	0.4498	210	0.4538	315	0.4578
				320	0.4580

[1] *Loc. cit.*

Thus a solution containing 100 milligrams of mixed carbohydrates, using the factor 0.00386, if it formed 200 milligrams cupric oxide by reduction of the Fehling solution in the manner above described, would have a cupric reducing power, or $K_{3.86}$ of 90.68.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

ALUMINUM ANALYSIS.

BY JAMES OTIS HANDY.

Received June 30, 1896.

ALTHOUGH the aluminum industry is not a large one in the sense that the iron industry is, it is growing very rapidly. The output of the United States in 1894 was 550,000 pounds, and in 1895 it was about 850,000 pounds. The Pittsburg Reduction Company, with works at New Kensington, near Pittsburg, Pa., and at Niagara Falls, N. Y., is the only American producer of aluminum. The material is made by the electrolysis, in carbon-lined pots, of alumina dissolved in a fused bath of fluorides. The product of each pot is ladled out at intervals and is graded according to the analyses of the Pittsburgh Testing Laboratory, Limited. Some of the aluminum is sold as it is made and some is alloyed to modify its physical properties. Alloys of aluminum with three per cent. nickel, or with three to seven per cent. copper, or similar amounts of zinc are very useful on account of increased strength with only slightly increased specific gravity. The aluminum at present produced with the best ores available contains from

99 to 99.9 per cent. of aluminum.
0.3 to 0.05 per cent. of silicon (combined and graphitic).
0.50 to 0.0 per cent. of copper.
0.20 to 0.0 per cent. of iron.
Carbon is sometimes present in aluminum.

Second grade aluminum contains ninety-six to ninety-eight per cent. aluminum, silicon and iron making up the remainder. Aside from analyses of metallic aluminum, there are required in the pursuit of the aluminum industry, analyses of alloys of copper, nickel, manganese, chromium, tungsten, zinc, and tita-

nium, with aluminum; aluminum solders, containing tin, zinc, and phosphorus; aluminum hydrate, bauxite, and electrode carbons; hydrofluoric acid and fluorides.

ANALYSIS OF COMMERCIAL ALUMINUM. (95 to 99.9 PER CENT. PURE).

In the analysis of aluminum we are offered a choice of solvents.

Solubility of Aluminum: Hydrochloric acid of thirty-three per cent., (*i. e.*, one part of hydrochloric acid of 1.2 sp. gr. to two parts water) is a rapid solvent.

Sulphuric acid of twenty-five per cent. dissolves aluminum completely on long boiling.

Nitric acid of one and two-tenths specific gravity dissolves aluminum on prolonged boiling.

Acid mixture: A mixture of the three acids which we term "Acid Mixture" is made of

100 cc. nitric acid of 1.42 sp. gr.
300 cc. hydrochloric acid of 1.20 sp. gr.
600 cc. sulphuric acid of twenty-five per cent.

It is a very useful solvent for aluminum because it supplies oxidizing conditions during solution and so prevents loss of combined silicon as hydride. The sulphuric acid content of the acid mixture furnishes a means of rapidly dehydrating the silica.

Sodium hydroxide solution of thirty-three per cent. is a useful solvent when it is desired to separate the metallic impurities from the bulk of the aluminum at once. Weaker solutions do not work as quickly or completely. Solution succeeds best in an Erlenmeyer flask.

Fifteen cc. of the sodium hydroxide solution suffice for one gram of aluminum.

Commercial soda lye may be used if dissolved and filtered through asbestos.

OTHER REAGENTS AND STANDARD SOLUTIONS USED IN ALUMINUM ANALYSIS.

Sodium carbonate, chemically pure.

Soda ash: "Solvay" soda ash, a saturated solution in water, filtered.

Powdered zinc : Practically free from iron and copper.

Fifteen per cent. nitric wash : (Fifteen parts 1.42 nitric acid to eighty-five parts water).

Standard potassium permanganate : 5.76 grams in two liters. One cc. equals 0.005 grams iron.

Standard potassium cyanide: Forty-five grams in two liters. One cc. is made to equal 0.005 gram coppper.

SPECIAL APPARATUS.

Two narrow glass tubes, graduated roughly, one to hold one gram of powdered zinc and the other one gram of chemically pure sodium carbonate.

The evaporating dishes which are used are, preferably, about four and a half inches in diameter, and are covered with five-inch glasses.

The Erlenmeyer flasks are of about twelve ounce capacity and furnished with porcelain crucible covers.

THE METHOD.

Determination of Silicon, Iron, and Copper in Commercial Aluminum.—One gram of aluminum drillings is dissolved in a four and a half inch evaporating dish in thirty cc. of "acid mixture." If the drillings are thin it is best to add only fifteen cc. at first. Placing cold water on the cover glass sometimes prevents loss from too energetic foaming. Solution having been completed by warming slightly, evaporate quickly to strong fumes of sulphuric acid and continue heating for five minutes. Experience will show on what parts of the hot plate these solutions can be evaporated without spattering at the time when aluminum sulphate begins to crystallize out. Remove the dishes from the plate by means of an iron fork, and in a few moments add to the contents of each seventy-five to 100 cc. of water and ten cc. of twenty-five per cent. sulphuric acid, break up the residue in each dish with a short, heavy glass rod, and place the dishes back on the hot plate. Boil until all aluminum sulphate dissolves. Add to each dish one gram of metallic zinc powder, measured. Be careful to pour the zinc into the middle of the liquid. If it touches the sides of the dish it sometimes

becomes firmly fixed there. Keep the dish contents at 60° to 70° C. until the zinc has dissolved, leaving the iron reduced and the copper precipitated. Filter and wash well with hot water. Cool, titrate the filtrates with standard potassium permanganate. One cc. equals 0.50 per cent. iron when one gram of aluminum has been used. Placing new receivers under the funnels, treat each residue twice with hot fifteen per cent. nitric acid wash. Wash out with water, and in the solutions thus obtained, titrate the copper with standard potassium cyanide, after adding saturated soda ash solution until the precipitated copper carbonate redissolves. The end point of the titration is very satisfactory. The cyanide solution should be standardized with copper of known purity in about the amount usually found, *viz.*, 0.005 to 0.010 gram. The residue of silicon and silica are burned off in numbered crucibles and each fused with one gram of chemically pure sodium carbonate (measured). The crucible containing the fused mass is placed in fifteen cc. of water in the porcelain dish originally used, and twenty-five cc. of twenty-five per cent. sulphuric acid are added. Solution takes place quickly without separation of silica, and after rinsing out and removing the crucible, the solution is evaporated to five minutes fuming on the hot plate. After cooling add seventy-five to 100 cc. of water and boil to disintegrate the silica. Filter and wash well with water. Burn off and weigh silica and crucible, treat with hydrofluoric acid and a drop of sulphuric acid if impurity is suspected. Evaporate, ignite, and weigh again. Loss equals silica; calculate to silicon.

Determination of Crystalline (Graphitic) Silicon in Aluminum.—Dissolve one gram of aluminum in thirty cc. of thirty-three per cent. hydrochloric acid (two parts of water to one of hydrochloric acid) in a platinum dish; add about two cc. of hydrofluoric acid, stir, and filter at once through a No. 0 nine cm. filter, contained in a funnel which has been thinly coated with paraffin. Wash with water and burn off in a platinum crucible. Fuse with one gram of sodium carbonate, cool in fifteen cc. of water in a four and a half inch evaporating dish. Add twenty cc. of twenty-five per cent. sulphuric acid. Rinse out the crucible. Evaporate to fumes, cool, add seventy-five cc. of water,

boil up and filter off the silica. Wash, ignite, and weigh. Calculate to silicon.

The determinations of silicon, copper, and iron are the every day methods of grading aluminum. It is recognized that sodium and carbon occasionally exist in aluminum, and they are determined by methods described. In certain samples it is desirable to know the approximate percentage of graphitic and combined silicon. These determinations are also described. We determine nitrogen, if present, by a special method.

DETERMINATION OF SODIUM IN ALUMINUM.

One gram of drillings is dissolved in a porcelain evaporating dish in fifty cc. of 1.3 sp. gr. nitric acid and sufficient hydrochloric acid to effect solution. Boil down until all hydrochloric acid has been removed. Rinse the solution into a large platinum dish and evaporate to dryness. Heat over a good Bunsen burner until nitric oxide fumes cease to be evolved. Grind the residue finely. Mix it by grinding with one gram of chemically pure ammonium chloride and eight grams of chemically pure calcium carbonate. Heat the mixture in a large covered platinum crucible. For the first fifteen minutes have a Bunsen burner flame just touching the bottom of the crucible, and for the next forty-five minutes, have the whole crucible heated bright red by a full Bunsen burner flame. Cool, and treat the residue with hot, distilled water until it becomes just friable under pressure. Avoid adding an excess of water beyond that necessary to make the sintered mass just friable. Grind it in a wedgewood mortar and rinse out with hot distilled water. Filter, rejecting the well washed residue, and treat the filtrate at the room temperature with saturated ammonium carbonate solution in slight excess. Stir very thoroughly. The precipitated calcium carbonate is at first flocculent, but on standing for about ten minutes, it becomes crystalline. Filter into a platinum dish; reject the residue and evaporate the solution on the water-bath to dryness. Heat carefully to dull redness to expel ammonium salts. Dissolve the residue in a little water and add a few drops of ammonium carbonate solution. If this produces a precipitate, add sufficient ammonium carbonate solution to precipitate all of the

remaining lime. Stir well, wait ten minutes, filter, evaporate to dryness, heat to dull redness, and weigh sodium chloride. Deduct any sodium chloride found in a blank determination, using acids, etc., as above, and finally eight grams of calcium carbonate and one gram of ammonium chloride.

$$NaCl \times 0.39316 = Na.$$

Care should be taken when heating up the residue of sodium chloride, etc., after evaporating on the water-bath. If the platinum dish and contents are heated for a few minutes on sheet asbestos on the hot plate before placing over the lamp, spattering may be avoided. Sodium is generally absent from aluminum, but it has been found in amounts as high as 0.20 per cent. and is considered a cause of the occasional deterioration of the metal in water.

DETERMINATION OF CARBON IN ALUMINUM. (MOISSAN'S METHOD MODIFIED.)

Triturate two grams of drillings in a Wedgewood mortar with ten to fifteen grams of mercuric chloride, powdered and dissolved, or partly dissolved, in about fifteen cc. of water. Reaction takes place rapidly and a heavy gray residue is left. Persistent trituration removes the last particles of metallic aluminum. Evaporate on the water-bath to dryness. The dry residue is heated in a current of pure hydrogen to expel mercuric compounds. The remaining material is then placed in a boat in a combustion tube and burned off as in carbon determination in steel. The carbon dioxide is caught as barium carbonate, and the excess of barium hydroxide determined by means of standard acid. We are working on a more generally applicable method for carbon in aluminum.

DETERMINATION OF NITROGEN IN ALUMINUM.

Aluminum, when overheated in re-melting, is believed to have the property of combining with nitrogen. The metal becomes weaker. Moissan's method for determining nitrogen in aluminum may be found in *Compt. Rend.*, 119, 12. Nitrogen thus absorbed would undoubtedly exist as nitride of aluminum and solution of sodium hydroxide with subsequent distillation

would seem to be the best method of procedure. We are working up this method.

DETERMINATION OF ALUMINUM IN METALLIC ALUMINUM.

Dissolve one gram of metal in thirty cc. of thirty-three per cent. hydrochloric acid in a porcelain dish and evaporated cautiously to complete dryness. Redissolve, by boiling, with ten cc. of concentrated hydrochloric acid and seventy-five cc. of water. Wash into a twelve ounce beaker; dilute to 250 cc. and pass hydrogen sulphide until saturated. Filter into a beaker and boil off hydrogen sulphide. Oxidize by adding one cc. of concentrated nitric acid and continuing to boil for ten minutes. Cool and make the solution up to 500 cc. Remove fifty cc. of the solution, and having diluted to 250 cc. and heated to boiling, add ammonium hydroxide in slight excess and boil well for twenty minutes. Let settle; filter, and wash thoroughly with hot water. It is necessary to wash the precipitate off from the filter, break it up, and wash it back again. Finally burn off in a thin-walled platinum crucible, igniting most intensely, and weighing the instant the crucible and content are cool. We have found that alumina is one of the most difficult oxides to dehydrate completely, and when dehydrated it absorbs atmospheric moisture even more rapidly than calcium oxide does. Moissan prefers to precipitate aluminum by ammonium sulphide. Having prepared a solution in hydrochloric acid, he takes an amount equal to 0.15 gram of aluminum, neutralizes it in the cold with ammonia, and precipitates it by ammonium sulphide, which has been recently prepared. He then digests for one hour, filters, washes with hot water, ignites and weighs.

ANALYSIS OF ALLOYS OF ALUMINUM WITH SMALLER AMOUNTS OF OTHER METALS.

Copper Alloys.—Three to thirty per cent. copper, and no zinc or nickel.

Dissolve one-half gram or one gram in fifteen cc. of thirty-three per cent. sodium hydroxide solution in an Erlenmeyer flask of twelve ounce capacity. If the flask is covered and set in a warm place, solution is complete in a few minutes, even if

the drillings are quite coarse. Dilute to thirty cc. with hot water and filter through a coarse, lintless filter paper (Whitall, Tatum & Co.'s five inch). Wash well with hot water. Dissolve residue, after washing it off the filter paper into a twelve ounce beaker, by warming with five cc. of concentrated nitric acid. Cool, add saturated commercial sodium carbonate solution until re-solution occurs. Titrate with standard potassium cyanide solution to the disappearance of the blue color. Standardize the cyanide for about the same amount of copper.

For commercial reasons, twenty per cent. alloys are made in the reduction pots, and these alloys are subsequently used for making copper alloys of low percentage.

DETERMINATION OF NICKEL IN ALUMINUM ALLOYS.

The three per cent. nickel alloy is now used. The addition of three per cent. of nickel increases the tensile strength of aluminum by several thousand pounds per square inch.

One gram of drillings is dissolved in fifteen cc. of thirty-three per cent. sodium hydroxide solution in a twelve ounce Erlenmeyer flask. Dilute to fifty cc. and filter through a five-inch lintless paper, washing the residue thoroughly with hot water. Rinse the residue back into the flask and add three to five cc. of concentrated nitric acid, and a drop of concentrated hydrochloric acid. Boil, and when dissolved, cool, and make up to 250 cc. In 100 cc. determine the copper by neutralizing with ammonia, adding two cc. of concentrated hydrochloric acid, warming and passing hydrogen sulphide. Filter and wash with ammonium sulphide. Burn it off carefully in a porcelain crucible, and having weighed, dissolve in five cc. of concentrated nitric acid. Then dilute to twenty cc., add excess of sodium carbonate solution and titrate with standard potassium cyanide. Boil the filtrate from the cupric sulphide, oxidize with one cc. of nitric acid, and precipitate with ammonium hydroxide. Do not boil, but digest for a few minutes just below the boiling point. Filter, wash, redissolve in hot fifteen per cent. nitric acid wash. Dilute to 150 cc. and again precipitate with excess of ammonium hydroxide, being careful to avoid boiling or prolonged digestion. Filter and wash. Burn off and weigh ferric oxide, etc. In a second

100 cc. of the main solution, precipitate nickel hydroxide, cupric oxide, ferric hydroxide, etc., by thirty-three per cent. chemically pure sodium hydroxide solution, added in slight excess to the boiling solution. Boil for fifteen minutes, filter, and wash most thoroughly with hot water. Burn off and weigh nickel oxide, cupric oxide and ferric oxide. Deduct cupric oxide and ferric oxide already found. Calculate nickel oxide to metallic nickel.

ANALYSIS OF ALUMINUM-MANGANESE ALLOYS.

Determination of Manganese.—Place one gram of drillings in a twelve ounce beaker. Add thirty cc. of thirty-three per cent. hydrochloric acid (one part of concentrated hydrochloric acid to two of water). When dissolved, add twenty-five cc. of nitric acid (1.42), and boil down to ten cc. Add fifty cc. of colorless nitric acid (1.42) and boil. Precipitate the manganese with powdered potassium chlorate, added cautiously, and proceed as described under manganese in steel by Williams' method.[1]

ANALYSIS OF CHROMIUM-ALUMINUM ALLOY.

Determination of Chromium.—Dissolve one gram in a twelve ounce beaker in thirty cc. of thirty-three per cent. hydrochloric acid, and when dissolved add fifty cc. of sulphuric acid (1.84), and evaporate carefully until fumes of sulphur trioxide escape. Cool, add sixty cc. of water and boil. After five minutes, if all aluminum sulphate has been dissolved, add powdered potassium permanganate until the solution has a distinct pink color. Boil until the excess of potassium permanganate is decomposed. Filter through washed asbestos and determine the chromium in the filtrate as in chrome steel.[2]

ANALYSIS OF TUNGSTEN-ALUMINUM ALLOY.

Determination of Tungsten.—Dissolve one gram in thirty-three per cent. hydrochloric acid in a four and a half inch evaporating dish. Add thirty cc. of nitric acid (1.42) and evaporate to dryness. Redissolve in thirty cc. of hydrochloric acid (1.20), dilute to about ninety cc., and boil for two hours. Filter and wash thoroughly. Burn off and weigh $Si + SiO_2 + WO_3 +$ crucible. Treat with three drops of twenty-five per cent. sul-

1 Blair's "Chemical Analysis of Iron."

2 Galbraith's Method. See Blair's "Chemical Analysis of Iron."

phuric acid and about two cc. of hydrochloric acid. Evaporate carefully over an Argand burner, re-ignite, and weigh crucible and silicon and tungstic oxide. Fuse with one gram of sodium carbonate, cool, place in dish, and add fifteen cc. of water and twenty cc. of twenty-five per cent. sulphuric acid, remove crucible and evaporate until white fumes escape. Cool, redissolve in about fifty cc. of water. Filter, wash, ignite, and weigh silica (from silicon), tungstic oxide, and crucible. Treat with sulphuric acid and hydrofluoric acid, evaporate, ignite, and reweigh. Loss equals silica. Calculate to silicon and add to the weight of silica lost by treatment of first insoluble residue. Deduct this sum from the weight of silicon, silica, and tungstic oxide first found and the remainder equals tungstic oxide. Calculate to tungsten.

ANALYSIS OF ALUMINUM-TITANIUM ALLOY.

Determination of Titanium.—Two grams of the alloy in a twelve ounce Erlenmeyer flask are dissolved by addition of fifty cc. of ten per cent. potash solution. Dilute with distilled water to about 125 cc., boil up, and filter as quickly as possible. Wash ten times with boiling water. Burn off the residue in a porcelain crucible, crush it in a Wedgwood mortar, fuse in a large platinum crucible with ten grams of potassium bisulphate. Conduct the fusion exactly as follows: Choose a good Bunsen burner, and protect it from draught by a sheet-iron chimney; make the flame one and a half inches long, and place the triangle carrying the upright crucible just at the point of the flame. Increase the heat gradually until in ten minutes the lower fourth of the crucible is red hot. Allow it to remain at this temperature ten minutes, moving the lid slightly to one side every two minutes, and giving the crucible (held firmly in the tongs) a gentle rotating movement, then turn up the light until the flame reaches the top of the crucible and envelopes it. Five minutes of this treatment melts down any potassium bisulphate, etc., which have risen on the sides. The flame is lowered and the lower fourth heated for ten minutes longer. Cool, dissolve in about 200 cc. of water; filter, rejecting the residue, if ignition and treatment with hydrofluoric acid show it to be only silica.

If it contains anything more, fuse with four grams of potassium bisulphate again. The filtrate contains all the titanic oxide and the ferric oxide. Add ammonia until a slight permanent precipitate is formed, then add dilute sulphuric acid from a pipette or burette until this precipitate just redissolves. Finally add one cc. more of twenty-five per cent. sulphuric acid and dilute to 300 cc. If the solution is high in iron (which will be indicated by its distinct yellow color) sulphur dioxide gas must be run into it until it is decolorized and smells strongly of sulphur dioxide, but if the solution is nearly colorless, indicating a low percentage of iron, only sulphur dioxide water need be added for the reduction. Boil well for one hour, adding water saturated with sulphur dioxide occasionally. Filter off the titanic oxide through double filters and wash well with hot water. Burn off and weigh as titanic oxide. If the precipitate is yellow, indicating the presence of iron, it may be fused with one gram of potassium bisulphate, the fusion dissolved in ten cc. of dilute sulphuric acid, and the iron determined in this solution by reducing with one gram of zinc, and titrating with permanganate. This is not often necessary. Calculate titanic oxide to titanium. $TiO_2 \times 0.6 = Ti$.

DETERMINATION OF ZINC IN ZINC-ALUMINUM ALLOY. FIRST METHOD.

Dissolve one gram in thirty cc. of thirty-three per cent. hydrochloric acid in a twelve ounce beaker. Dilute to 200 cc. and heat nearly to boiling. Pass hydrogen sulphide till all copper is precipitated. Filter and boil off hydrogen sulphide, oxidize with one cc. nitric acid by boiling ten minutes. Add sodium hydroxide solution until neutral, then make barely acid with hydrochloric acid, and stir until the aluminum hydroxide all dissolves. Add ten grams of sodium acetate and 500 cc. of water, boil up, and filter at once. Dissolve the washed precipitate in hydrochloric acid and repeat the acetate separation. Heat the united filtrates to boiling and pass hydrogen sulphide. Filter off the zinc sulphide on double filters, wash thoroughly with hot water. Burn off in a porcelain crucible, and weigh zinc oxide. Calculate to zinc. This method may be used when

obtaining in this way the total solids. For this purpose an arbitrary value is taken which shall represent the influence of one gram of a mixture of the three substances above mentioned on the specific gravity if dissolved to 100 cc. in distilled water. Brown and Heron[1] claim that this influence on the specific gravity of one gram starch conversion product in 100 cc. is 0.00386. This value has been determined to be correct for solutions of cane sugar, and is much used for glucose work.

As above mentioned the specific gravity of a dextrose solution containing ten grams dextrose anhydride in 100 cc. is 1.03809 at 15.5°. To determine the cupric reducing power of a substance using the value 3.86 as a divisor, it therefore becomes necessary to change the figures given in the tables to conform to this new factor, that is, the dextrose equivalents must be multiplied by $\frac{386}{381}$, which has been done for convenience of reference in the following table:

Copper oxide obtained.	Dextrose equivalent.	Copper oxide obtained.	Dextrose equivalent.	Copper oxide obtained.	Dextrose equivalent.
5	0.4461	110	0.4500	215	0.4540
10	0.4463	115	0.4502	220	0.4542
15	0.4465	120	0.4504	225	0.4543
20	0.4467	125	0.4506	230	0.4545
25	0.4468	130	0.4508	235	0.4547
30	0.4470	135	0.4510	240	0.4549
35	0.4472	140	0.4512	245	0.4551
40	0.4474	145	0.4513	250	0.4553
45	0.4476	150	0.4515	255	0.4555
50	0.4478	155	0.4517	260	0.4557
55	0.4480	160	0.4519	265	0.4558
60	0.4482	165	0.4521	270	0.4560
65	0.4484	170	0.4523	275	0.4562
70	0.4485	175	0.4525	280	0.4564
75	0.4487	180	0.4527	285	0.4566
80	0.4489	185	0.4528	290	0.4568
85	0.4491	190	0 4530	295	0.4570
90	0.4493	195	0.4532	300	0.4572
95	0.4495	200	0.4534	305	0.4574
100	0.4497	205	0.4536	310	0.4576
105	0.4498	210	0.4538	315	0.4578
				320	0.4580

1 *Loc. cit.*

complete dryness on a hot plate. Cool, add twenty-five cc. of nitric acid (1.13), and boil thoroughly. Filter. The residue contains all of the tin, most of the phosphorus, and possibly some zinc. Burn it off in a porcelain crucible and, after pulverizing the residue in an agate mortar, mix it with two grams of sodium carbonate and two grams of sulphur, fuse it in a covered porcelain crucible over a Bunsen burner for about half an hour. Give it three minutes of gentle blast flame at the last. Cool, boil out with 150 cc. of water in a twelve-ounce covered beaker. Filter and wash. Extract any possible zinc sulphide, etc., from the residue, by dissolving in nitric acid, boiling off hydrogen sulphide, and adding this to the first filtrate obtained after evaporating to dryness with nitric acid. The sodium sulphide solution contains the tin and phosphorus. Add to it hydrochloric acid until just acid. Warm slightly and pass hydrogen sulphide. Filter off stannous sulphide and wash thoroughly with hot water. Burn off in a porcelain crucible and weigh stannic oxide. Calculate to metallic tin. The filtrate from the stannous sulphide is boiled to expel hydrogen sulphide and then oxidized by adding two cc. of nitric acid and boiling for fifteen minutes more. Filter off any sulphur which separates, and in this filtrate, which should amount to only about 100 cc., precipitate the phosphorus by adding pure sodium hydroxide solution till alkaline, then nitric acid till distinctly acid, heating to 85° C., and adding fifty cc. of filtered molybdate solution. Stir or shake well for five minutes, filter on a weighed filter paper, and after washing with one per cent. nitric acid wash, dry at 100° C. and weigh. Yellow precipitate multiplied by 0.0163 equals phosphorus. The nitric acid solution obtained after evaporating the first solution to dryness, etc., is now neutralized with sodium hydroxide solution, and then made just acid with hydrochloric acid. Ten grams of sodium acetate are now added, and 300 cc. of water (hot). Boil up for five minutes, then filter and wash. If the precipitate is of considerable size, it is probable that aluminum was a constituent of the solder. Redissolve it in a little hydrochloric acid, neutralize, acidify, and make a basic acetate separation as before. Precipitate the zinc in the acetate solutions by hydrogen sulphide.

Filter, wash, ignite in a porcelain crucible, and weigh as zinc oxide. Calculate to metallic zinc. Dissolve the precipitate of aluminum acetate in hydrochloric acid, dilute to 250 cc., and precipitate with ammonia. After filtering, washing, igniting, and weighing as alumina, calculate to metallic aluminum. Solders containing lead are sometimes met with. In such cases, evaporate the nitric acid filtrate from the metastannic acid to small bulk, add twenty-five cc. of twenty-five per cent.. sulphuric acid, and evaporate until white fumes escape. Cool, add 100 cc. of water, stir, and let stand for an hour in a warm place. Filter and wash with water containing five per cent. of sulphuric acid. Burn off in a porcelain crucible at a low temperature. Reoxidize any reduced lead oxide and restore its sulphur trioxide by adding a few drops of nitric acid and sulphuric acid and evaporating. Finally weigh lead sulphate. Calculate to metallic lead. Zinc is determined in the lead sulphate filtrate.

ANALYSIS OF ALUMINA.

Alumina is made from bauxite or cryolite. It is usually purchased in the hydrated form.

HYDRATED ALUMINA.

Hydrated alumina is analyzed for water, silica and sodium carbonate.

Water.—Ignite one gram in a closely covered crucible, at first gently and then intensely for fifteen minutes over the strongest blast. The loss on ignition includes water and the carbon dioxide of the sodium carbonate. Calculate the carbon dioxide from the sodium oxide found and deduct it from the loss on ignition.

Silica.—Hydrated alumina is soluble in sulphuric acid of 42° B. The silica, however, is left undissolved. 42° B. sulphuric acid is made by mixing 900 cc. of concentrated sulphuric acid with 1290 cc. of water. Five grams of hydrated alumina are treated with twenty-five cc. of 42° B. sulphuric acid and heated until the alumina appears to be all dissolved. Dilute to 100 cc. and boil. Filter, wash, ignite and fuse the residue with one gram of potassium bisulphate and cool. Dissolve in water, filter, wash, ignite, and weigh in cru-

cible, treat with sulphuric acid and hydrofluoric acid, evaporate, ignite and weigh again. Loss equals silica.

Soda.—The method for the determination of soda is the same in calcined and hydrated alumina. The method is that of J. L. Smith, and is described under "Sodium in Aluminum." Calculate sodium chloride to sodium carbonate, if the sample is hydrated, and to sodium oxide if the sample is calcined alumina.

CALCINED ALUMINA.

Water and soda are determined as in hydrated alumina.

Silica.—Fuse one gram of the finely ground alumina with ten grams of potassium bisulphate. If this does not make a clear fusion add two grams of bisulphate and heat up again. Dissolve the fusion when cool in water and filter. Burn off the insoluble residue. Fuse it with one gram of sodium carbonate and cool in fifteen cc. of water in a four and a half inch evaporating dish. Add twenty-five cc. of twenty-five per cent. sulphuric acid. When all soluble matter has dissolved, remove the crucible and evaporate down until sulphuric acid fumes escape. Cool, dilute with water, boil, filter, ignite, and weigh silica plus crucible, treat with sulphuric and hydrofluoric acids, and weigh again. Loss equals silica.

ANALYSIS OF BAUXITE.

Method adopted, May, 1895.

No unusual apparatus or reagents are required.

One and five-tenths grams of very finely ground bauxite (previously dried at 100° C. and bottled), is taken for analysis. Weigh into a five inch porcelain evaporating dish and dissolve in fifty cc. of acid mixture. This mixture is the same as that used for aluminum analysis. Boil the solution down until fumes escape and keep the residue fuming strongly for about fifteen minutes. Cool, add 100 cc. of water, stir and then boil for ten minutes. Filter, wash well with water, receiving the filtrate in a beaker of about 300 cc. capacity. The filtrate and washings should amount to about 175 cc. Burn off the insoluble residue (which consists chiefly of silica, with a little titanic acid, oxide of iron, and alumina) and weigh it in the crucible, add three drops of twenty-five per cent. sulphuric acid and about five cc. of hydro-

fluoric acid and evaporate slowly to dryness. Ignite very strongly and weigh. The loss in weight equals silica. Add to the residue in the crucible one gram of potassium bisulphate and fuse quickly and thoroughly over a Bunsen burner, cool and place the crucible in the beaker containing the main sulphuric acid solution. The small residue from this fusion will be silica, and is to be added to the silica already found. Having obtained the sulphate solution containing all the alumina, ferric oxide and titanic oxide, make it up to 550 cc. and mix. Then fifty cc. will equal three-tenths gram bauxite. Take fifty cc. and dilute to 300 cc. Add two cc. of concentrated hydrochloric acid and ammonia in slight excess, boil for five minutes, let the precipitate settle, filter and wash very thoroughly with hot water. Test the filtrate for further alumina by boiling. Burn off the filter paper and ignite the precipitate very strongly after crushing all the lumps of alumina. Weigh alumina, ferric oxide and titanic oxide.

Titanic Acid.—Take 100 cc. of the original sulphate solution (six-tenths gram), add ammonia until a slight permanent precipitate is formed, then add sulphuric acid from a pipette or burette until this precipitate just redissolves. Finally add one cc. more of twenty-five per cent. sulphuric acid and dilute to 400 cc. If the bauxite is high in iron (which will be indicated by the distinct yellow color of this solution) sulphur dioxide gas must be run into it until it is decolorized and smells strongly of sulphur dioxide, but if the solution is nearly colorless, indicating a low percentage of iron, only sulphur dioxide water need be used for the reduction. Boil well for one hour, adding water saturated with sulphur dioxide occasionally. Filter off the titanic oxide through double filters and wash well with hot water. If the precipitate is yellow, indicating the presence of iron, it can be fused with one gram of potassium bisulphate, the fusion dissolved in water, and the iron determined in this solution by reducing with zinc and titrating with permanganate. This is not often necessary.

Oxide of Iron.—Take fifty cc. of the sulphate solution, add ten cc. of dilute sulphuric acid and one gram of granulated zinc,

and set the beaker in a warm place. When reduced, filter and titrate the iron with standard potassium permanganate. More zinc is used for bauxites high in iron.

METHOD FOR IRON DETERMINATION, USING A LARGER QUANTITY OF BAUXITE. (APPLICABLE TO PUREST ORES).

Place a half gram of the finely powdered ore in a large platinum crucible and add three cc. of twenty-five per cent. sulphuric acid and five cc. of hydrochloric acid, and evaporate very slowly to fumes; drive off the excess of sulphuric acid by heat, boil out the residue with water and add ten cc. of dilute sulphuric acid. Remove the crucible and reduce with zinc, as above, and titrate.

Water and Organic Matter.—Ignite three-tenths gram, cautiously at first and finally very strongly in a covered crucible. The loss of weight equals water and organic matter.

ESTIMATION OF THORIA. CHEMICAL ANALYSIS OF MONAZITE SAND.

BY CHARLES GLASER.

Received July 9, 1896.

SINCE the introduction of the Auer-Welsbach light, the commercial importance of monazite sand has grown greatly, and chemists are now asked to determine the percentage of true monazite, and especially that of thoria, in samples of the sand. This has heretofore been accomplished indirectly; the quantities of iron, titanium and silica were determined and the remainder of the material calculated as monazite. A sample treated in this manner gave the following results:

	Per cent.
Iron oxide	3.50
Titanic acid	4.67
Silica	6.40
Monazite, by difference	85.43
	100.00

The sample contained 18.38 per cent. phosphoric acid, which calculated as cerium phosphate (factor 3.32) equals 61.10 per cent.

From analyses printed in Dana's Mineralogy, it was inferred

that after elimination of rutile and silica, the remainder would be found to consist chiefly of phosphates of the cerium group, but this is not true.

For the determination of the actual composition of the monazite sand in question, it was decided to attempt an estimation of each of its components, by means of methods to be found in the available literature. As chief sources of information, Graham-Otto's Chemistry and Crookes' Select Methods in Chemical Analysis were used; due regard was also given to the work which has appeared in the chemical journals of recent years. I was not able, however, to make an exhaustive examination of the literature.

It became evident that no reliable method could be worked out until examination had been made of all the work which had been done in the field, and it seemed necessary to investigate the whole question. In the following statements of preliminary experiments a large portion of analytical data has been omitted, because otherwise this paper would have been bulky. Only the outlines of a general plan of procedure will therefore be given.

So far as possible, it was my intention to examine all the methods proposed for estimation of thoria, but in one notable instance this could not be done. In Volume XVI of the *American Chemical Journal*, L. M. Dennis and F. L. Kortright describe a method for estimation of thoria by means of potassium hydronitride, KN_3. An attempt to work by the method proved a failure in my hands, partly because of a mishap while preparing the reagent, only enough of which was saved for a single qualitative reaction; but chiefly because Mr. Dennis declined, when requested, to give me further information. He replied that he was not then at liberty to detail his experience, "as the potassium hydronitride process is more than an analytical one. It is a commercial process for the preparation of pure thoria, which is, I think, unequalled by any of the methods employed by the Welsbach chemists, Shapleigh included. Some of them have tried to use the method and have failed. I think I know why they failed. But I do not think it quite fair for them to ask me to help them out of their difficulties."

Although the publication was made in a scientific journal, it

seems to have been but a partial statement. For which reason criticism is invited and the value of the work is thrown somewhat in doubt. No further attempt was made to follow it out.

By means of fusion with alkali carbonates, an attempt was made to separate monazite sand into two parts. According to Wöhler all titanic acid ought to become soluble provided the fusion is made at a sufficiently high temperature. Therefore a blowpipe was used. In later work I employed the highest temperatures afforded by a muffle, and for as many as two hours. But at no time was more than a fraction of the titanic acid rendered soluble in water. Moreover, Wöhler's directions to pour the fusion upon an iron plate, and afterwards to powder it, are not practicable because of loss likely to ensue. It was found best to let the fusion soak in water over night, sometimes even for several days, or until perfect disintegration resulted. But such a procedure may have decreased the solubility of titanic acid in water. Phosphoric acid and alumina (and also silica to a large extent) were completely dissolved out of the fused mass. The portion insoluble in water was rendered soluble by the well known treatment with strong sulphuric acid, and also by fusion with acid potassium sulphate. The solution thus obtained, after being freed from silica, was boiled to separate titanic acid, from four to seven hours during the first experiment. Later, after addition of sodium sulphite, this was accompanied by saturating with hydrogen sulphide, first in the hot and then in the cooled solution. This method is preferable to the first.

After separation of titanic acid and the metals of the fifth group, various methods were tried for separation of thoria from the other earths. It was found that the solution must not be strongly acid when treated with ammonium oxalate for precipitation of thoria and the metals of the cerium group, or traces of thoria will remain in solution. It is best to nearly neutralize with ammonia, and to precipitate in boiling solution.

During the earlier experiments some difficulty was found in keeping in solution all of the zirconia, which is accomplished only by a large excess of the reagent, while yttria and glucina readily form soluble double salts. Under these conditions oxalates of the cerium metals precipitate immediately, while thorium

oxalate separates upon cooling. Attempts to separate thorium oxalate from oxalates of the metals of the cerium group by filtration of the hot solution, gave unsatisfactory results. The oxalates will pass through the filter for a long time. Bumping of the liquid made it impracticable to keep it boiling until the entire precipitate became crystalline. But if large quantities of thoria are to be separated from small ones of the other oxalates the method works well.

After the insoluble oxalates were separated by filtration and were washed with water, they were converted into oxides by heating and were redissolved as sulphates. In this strongly concentrated solution, made nearly neutral by ammonia, an attempt was made to separate thoria from the other metals by boiling with sodium hyposulphite. In no instance was a complete separation effected, but such portions as were obtained proved to be quite pure. The single exception was that in which the whole of the cerium was precipitated, for reasons not ascertained. Attempts were made to free thoria from most of the cerium by fractional precipitation with weak ammonia, but no considerable advantage was gained thereby, since repeatedly the second fraction showed traces of thorium.

To determine the solubility or insolubility of the different substances left in the insoluble residue from fusions, such residue was treated with dilute hydrochloric acid both cold and hot. The solution was found to contain all the iron and titanium, the larger part of the silica, and about one-half of the earths present; these consisted of relatively large portions of zirconia and glucina. Thoria seems not to enter into solution, but is left with the remainder of the earths.

An attempt was made to separate thorium oxalate from the mixed precipitated oxalates, by boiling with ammonium oxalate. Such boiling, filtering and crystallizing yielded oxalates, which after ignition, corresponded to 2.29 per cent. of oxides. The earths were, however, of a deep orange color, and contained both cerium and zirconia. The latter was present because an insufficient quantity of ammonium oxalate had been used in the first precipitation. In the oxalates of the cerium metals found insoluble in the above treatment, the presence of thoria could be

distinctly proven by means of sodium hyposulphite, for which reason the work proved unsatisfactory.

To facilitate a comparison of the more important reactions of the elements herein studied, the table on the next page has been prepared partly from their known behavior, and partly from the results obtained during this investigation.

With the view of obtaining further knowledge of the behavior of thoria, fragments of Welsbach mantles were subjected to analysis. They weighed 0.6591 gram, which, after ignition, fell to 0.6552 gram. Prolonged treatment with boiling sulphuric acid left a residue of 0.0883 gram, which became soluble in water after fusion with acid potassium sulphate. The solutions thus obtained were examined by the same method, but separately, as follows: After neutralizing with ammonia the greater part of the free acid, the solutions were heated to boiling and hot solution of ammonium oxalate was added.

In solution I a precipitate appeared, but dissolved rapidly upon addition of more of the reagent.

In solution II a slight turbidity appeared, there was no precipitate, and it soon became perfectly clear.

Upon cooling, solution I yielded a moderate quantity of a crystalline deposit, while solution II gave a copious one. Both precipitates were collected on one filter, washed, ignited, and weighed. They yielded 0.1124 grams of thoria.

The filtrate from I gave a copious precipitate with ammonia, while that from II gave only a slight one: both of these were washed on one filter, redissolved in dilute hydrochloric acid, and again precipitated by ammonia. An excess of ammonium carbonate entirely dissolved the precipitate. Potassium hydroxide gave a precipitate not soluble in excess of the precipitant, indicating zirconia, the weight of which was 0.5580 gram. An attempt to purify it from occluded alkali, by again precipitating with ammonia, failed through an accident, in which part of the material was lost. Calculating by difference, the weight of zirconia ought to have been 0.5428 gram. Both precipitates were pure white.

Therefore, this analysis afforded the following composition of the mantles: thoria 17.15 per cent., zirconia 82.85 per cent.

Table of Reactions of the Rarer Earths.

	KOH or NaOH	K_2CO_3 or Na_2CO_3.	K_2SO_4 or Na_2SO_4.	$Na_2S_2O_3$.	NH_4OH.	$(NH_4)_2CO_3$.	NH_4Cl.	$(NH_4)_2C_2O_4$.	$NH_4C_2H_3O_2$.
Al_2O_3	Ppt., sol. in excess.	Ppt.	Alums.	Ppt. in boiling almost neutral solution.	Ppt.	Ppt.	Ppt. from solution in NaOH.	No ppt.	Nearly neutral solution boiled gives ppt. of basic salt.
BeO_2	Ppt. sol. in excess. Reppt. when boiled or diluted.	Ppt. with difficulty sol. in large excess and in CO_2.	No ppt., no double salt formed. Sol. with difficulty.	No. ppt.	Ppt. insol. in excess.	Ppt. easily sol. in excess. Ppt. on boiling. Uncertain separation from Al_2O_3.	Hydroxide diss. on prolonged boiling NH_3 escapes.	No ppt., double salt easily sol.	?
ZrO_2	Ppt. insol. in excess.	Ppt. slightly soluble in excess. Ppt. by NH_4OH.	Double salt sol. in hot solution. Ppt. of basic salt on cooling, insol. in HCl.	Ppt. hydroxide mixed with S.	Ppt. insol. in excess.	Ppt. sol. in large excess. Repptd. on boiling.	No ppt.	Ppt. sol. in excess.	?
Gadolinite earths.	Ppt. insol. in excess.	Ppt. sol. in excess. After some hours insol. double salt separates (Yt).	Conc. solution ppt. sol. in H_2O or K_2SO_4 (not Yt.) Sept. from thoria and cerites.	?	Ppt. insol. in excess.	Ppt. easily sol. in excess. Ppt. insol. double salt after some hours (Yt).	?	Ppt. red granular powder (Er.) from boiling acid solution.	?
ThO_2	Ppt. insol. in excess.	Ppt. sol. in excess. Turbid on heating, clears on cooling.	Double salt insol. in saturated solution K_2SO_4. Sodium salt much more sol.	Only partial ppt., even on long boiling conc. solution.	Ppt. insol. in excess. ThO_2 ppts. before cerites. Crookes.	Like NH_4OH.	No ppt.	Ppt. nearly insol. in acids. Sol. in excess, hot; ppt. on cooling. HCl ppts.	No ppt. prevents completely ppt'n. by $(NH_4)_2C_2O_4$ Partial ppt. by HCl, complete by excess NH_4OH.
CeO	Ppt. insol. in excess.	Ppt. slightly sol. in excess.	Double salt insol. in K_2SO_4 solution.	No. ppt. (?)	Ppt. insol. in excess.	Like NH_4OH.	No ppt.	Ppt. even in rather acid solution. Slightly sol. in large excess of acid.	Oxalate insol.
Ce_2O_3	Excess gives flesh colored ppt.	Ppt. nearly insol. in excess.		No. ppt.	Like KOH.	Ppt. sol. in large excess. Repptd. on boiling.	No ppt.	Like CeO.	Oxalate insol.
La_2O_3	Ppt. insol. in excess.	Ppt. nearly insol. in excess.	Double salt sol. with difficulty.	No. ppt.	Ppt.	White ppt. quite insol. in excess.	No ppt.	Ppt. in neutral or ammoniacal (?) solution.	Oxalate insol.
Di_2O_3	Ppt. insol. in excess.	Ppt. nearly insol. in excess.	Double salt sol. with difficulty.	No. ppt.	Ppt.	Rose colored ppt. quite insol.	No ppt.	Ppt. nearly insol. in oxalic or mineral acids.	Oxalate insol.

The separation of the two earths was effected without difficulty and the thoria was used in the following experiments:

0.0487 gram was weighed, dissolved, and mixed with the solution of cerium metals from a previous experiment. The solution was nearly neutralized with ammonia, heated to boiling, a hot solution of ammonium oxalate added, and the mixture allowed to cool. The precipitate was caught on a filter and washed with cold water, extracted in boiling ammonium oxalate solution, caught on a filter, and washed hot: the filtrate was allowed to cool (precipitate 1). The residue was macerated in a hot solution of ammonium acetate, filtered (residue A), and filtrate examined for thoria, as follows: hydrochloric acid was added to separate thoria as oxalate, which fell in part only and the remainder was obtained by sodium hydroxide (precipitate 2). Both these precipitates afforded but a part of the thoria originally weighed, the greater part being held yet with the cerium metals. The method had failed.

The residue (A) upon the filter was reduced to oxide and dissolved as sulphate. After neutralizing with ammonia, the liquid was heated to boiling, and there was added an excess of ammonium oxalate with some ammonium acetate: after filtering, the filtrate was treated with sodium hydroxide (precipitate 3).

The precipitates, thus obtained in three fractions, were ignited and found to weigh 0.0774 gram, showing that the thoria was very impure. The grayish mass was fused with acid potassium sulphate, and unfortunately, a small fraction of the fused mass was lost. However, from the saved portion a pure thoria, weighing 0.0402 gram. was obtained.

In the next experiment, 0.0343 gram of thoria and 0.1004 gram of impure cerium oxide were dissolved as sulphates, and treated with ammonium oxalate and acetate, as for precipitate 3, next above. By precipitating the filtrate with ammonia there was obtained 0.0360 of impure thoria, which, after purification, weighed 0.0344 gram. Cerium oxide recovered weighed 0.0935 gram.

I desire to call attention to what has been observed frequently during these experiments. If thorium oxalate, held in solution

by ammonium acetate, be precipitated by ammonia, the earth so obtained, when washed with the greatest care and redissolved in a mineral acid, cannot from an almost neutral solution be again completely precipitated by ammonium oxalate; even if the earth had been ignited after re-solution. It will also be found that a considerable increase has occurred in its solubility in liquids containing much potassium or ammonium sulphate. When enough thoria has been collected, it is my intention to further examine this peculiar behavior.

SYSTEMATIC METHOD OF ANALYSIS.

From the analytical data given, the following method has been deduced:

It is essential that the mineral be divided to the greatest possible degree. Prolonged powdering in an agate mortar is indispensable. Solution is effected either by prolonged heating with strong sulphuric acid, or by fusion with acid potassium sulphate. In the latter case, the cooled mass is warmed with so much sulphuric acid that the product, after cooling, may be poured from the crucible. The first method takes more time than the second, but it introduces less of the objectionable potassium salts. It is advisable to fuse only those portions which are insoluble in sulphuric acid.

For estimation of silica the sulphuric acid treatment is preferable, in which case it is best to evaporate once on a sand-bath to dryness to render silica insoluble, and then to add fresh sulphuric acid. The resulting mixture should be added slowly to ice cold water, which dissolves the mass excepting silica and tantalic acid, with possibly traces of titanic acid, thoria, and zirconia. After filtering, the residue should be ignited and weighed. Silica is eliminated by repeated treatment with hydrofluoric acid. Any residue remaining should be moistened with sulphuric acid, to convert the fluorides of the earths into sulphates, which, after ignition at a high temperature, are weighed as oxides, and silica determined by the loss in weight. The residue of tantalic acid, with possibly traces of the bodies mentioned above, is treated with sulphuric acid and hydrofluoric acid. Tantalic acid remains insoluble, and may be filtered off

and weighed. The matter soluble may be added to the main solution.

The original solution is saturated with hydrogen sulphide, first at boiling and then at the ordinary temperature. Titanic acid is precipitated, together with metals of the fifth group. That sodium sulphite assists in the precipitation of titanic acid has not been verified in my work.

When completely settled, the liquid is filtered and the filtrate boiled to expel hydrogen sulphide. Any free acid may be nearly neutralized with ammonia ; to the boiling liquid is added an excess of a boiling solution of ammonium oxalate, as much as 100 cc. of the cold saturated solution for two grams of monazite sand. The excess necessarily must be large. The mixture is then permitted to cool, best for an entire night. The solution will contain phosphoric acid, the oxides of iron, manganese, aluminum, glucinum, yttrium, zirconium, and calcium. In the precipitate will be found thoria and the oxides of the cerium group.

If the bodies in solution are to be estimated, add ammonia to precipitate the metals as phosphates. Filter and wash thoroughly, preserve the filtrate for estimation of phosphoric acid and alumina. Ignite the precipitate and fuse it with mixed carbonates of potassium and sodium. The fused mass is exhausted with hot water, filtered, and the residue well washed with hot water. The filtrate is added to that containing phosphoric acid and alumina.

The remaining oxides and carbonates are dissolved in sulphuric acid and precipitated with ammonia. Lime is estimated in the filtrate therefrom.

When an attempt is now made to dissolve the precipitated hydroxides on the filter by dilute hydrochloric acid, it sometimes occurs that zirconia in part remains. Therefore it is best, after this operation, to incinerate the filter. Then neutralize the solution with ammonia as far as practicable. Pour this slowly, with constant stirring, into a mixture of ammonium carbonate and ammonium sulphide, prepared as follows : To a solution of ammonium carbonate more than enough to neutralize the free hydrochloric acid above indicated, and to hold in solution the

earths to be dealt with, add enough of ammonium sulphide (usually a few cc.) to precipitate the metals of the fourth group. The latter will be precipitated, while zirconia, yttria, and glucinum remain in solution. Iron and manganese may be determined by the usual methods.

If the carbonate solution be boiled for one hour the earths are completely precipitated. They may be caught on a filter and dissolved in hydrochloric acid; or the carbonate solution may be treated directly with that acid, carbon dioxide expelled by boiling, the solution cooled and treated with an excess of sodium hydroxide. Zirconium and yttria are completely precipitated while glucina remains dissolved: to precipitate this, boil the solution one hour.

To separate zirconia from yttria, dissolve the hydroxides in hydrochloric acid, warm, then saturate the solution with sodium sulphate. When cold, zirconia separates in the well-known manner. From the filtrate ammonia separates yttria.

As the earths are apt to occlude alkali salts, it is best to dissolve and again precipitate them (with ammonia) before they are ignited and weighed.

Separation of the precipitated oxalates of thoria and of the cerium group is accomplished as follows: The oxalates are reduced to oxides by ignition, then converted into sulphates, the greater part of the free acid neutralized with ammonia, the solution boiled, and boiling ammonium oxalate added in excess. After a short time (as soon as oxalates of the cerium metals have formed but before the liquid has cooled), a few cc. of solution of ammonium acetate are added. When cold, the entire cerium group is precipitated as oxalates, while thoria remains in solution. After prolonged standing, best over night, the insoluble oxalates are removed by filtration; in the filtrate, precipitate thoria with ammonia in excess, filter, ignite, and weigh.

Separation of cerium from lanthanum and didymium is easily accomplished by the well known method. Pass a current of chlorine through the liquid containing the hydroxides, which have been freshly precipitated by a fixed alkali.

Separation of lanthanum from didymium was not attempted.

An analysis of the monazite sand used in my work, made as indicated in the foregoing notes, gave results as follows:

Titanic acid	4.67
Silica	6.40
Phosphorus pentoxide	18.38
Lead	trace
Alumina	1.62
Lime	1.20
Cerium oxide (CeO)	32.93
Lanthanum and didymium oxides	7.93
Thoria	1.43
Ferric oxide	7.83
Zirconia and yttria	13.98
Glucina	1.25
Tantalic acid	0.66
Not determined	1.72
	100.00

Titanic acid and silica was determined in a separate portion.

The determination of tantalic acid was only approximate, since a part of it is dissolved by fusion with acid potassium sulphate, and thus escapes weighing. As several such fusions were made, it is probable that the greater part of the matter "not determined" ought to be reckoned as tantalic acid. The quantity stated was an average of three determinations (minus or plus 0.05) from the residue of repeated fusions.

Through the courtesy of Mr. H. B. C. Nitze, of the Geological Survey of North Carolina, I have received a number of samples of monazite sand mined at various localities in that state. Two of these had been prepared by a new process and were found to be practically free from rutile and garnets. They were excellent material for my methods of analysis, and they gave results as follows:

ANALYSIS OF A COARSE MONAZITE SAND FROM SHELBY, NORTH CAROLINA.

Silica	3.20
Titanic acid	0.61
Cerium metals as CeO	63.80
Phosphorus pentoxide	28.16
Thoria	2.32
Zirconia, glucina, yttria	1.52
Manganese	trace
No iron, alumina, or lime	0.00
	99.61

The color of this sand was honey-yellow.

ANALYSIS OF A FINE MONAZITE SAND FROM BELLEWOOD, NORTH CAROLINA.

Silica	1.45
Titanic acid	1.40
Cerium metals as CeO	59.09
Phosphorus pentoxide	26.05
Thoria	1.19
Zirconia, glucina, yttria	2.68
Tantalic acid	6.39
Iron and manganese oxides	0.65
Alumina	0.15
	99.05

The color of this sand was honey-yellow.

LABORATORY OF LEHMANN & GLASER,
BALTIMORE.

[CONTRIBUTIONS FROM METALLURGICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO.]

THE EFFECT OF AN EXCESS OF REAGENT IN THE PRECIPITATION OF BARIUM SULPHATE.

BY C. W. FOULK.

Received July 6, 1896.

"EXCESS of reagent" is a term often used by writers in quantitative chemistry, and the necessity in any given case for adding more of a precipitating reagent than is just sufficient for complete reaction is well known to analysts; but what constitutes such excess, whether it differs for different salts, whether its effect is counteracted by the presence in the solution of other bodies not taking part in the reaction, or whether the effect of such bodies may be counteracted by the addition of a greater amount of precipitant, etc., etc., are questions, the answers to which are difficult to find in chemical literature.

With a view to answer, in part at least, these questions, the following work on the precipitation of barium sulphate was undertaken.

A preliminary experiment, which perhaps is worth noting, was first tried :

A solution of 140 cc. water and five cc. concentrated hydrochloric acid was heated nearly to boiling and 0.1984 gram pure recently ignited barium sulphate was added. This was then stirred up and set aside for one hour, when it was filtered and

the barium sulphate washed well with hot water. The filter and the contents were then ignited and weighed, when it was found that ten milligrams of the sulphate had been dissolved. The filtrate was now divided, and to one-half some sulphuric acid was added, and to the other some barium chloride solution. *A precipitate of barium sulphate was produced in both cases.*

Standard solutions of sulphuric acid and barium chloride were now prepared. These were standardized by precipitation from pure water solutions.

The sulphuric acid used in this work was the chemically pure acid of the laboratory, tested for the ordinary impurities.

The barium chloride was recrystallized from the chemically pure salt.

The hydrochloric acid was the chemically pure acid of the laboratory tested for sulphuric acid.

The graduated ware was calibrated and found to be good.

All the precipitates of barium sulphate were ignited by folding up the moist filter, putting into a platinum crucible, "precipitate end" up and so adjusting the flame that the paper would be charred away without letting the crucible become red hot. Finally the heat was raised and the ignition finished. No lid was used on the crucible. By following this plan no reduction to sulphide need be feared.

A number of the precipitates were moistened with sulphuric acid and ignited. No change was noticed.

In the course of the work the following solutions were made:

SULPHURIC ACID SOLUTION.

Solution A.

	cc.	Barium sulphate.
1.	20	0.1978
2.	20	0.1975
3.	20	0.1970
4.	20	0.1978
	Average	0.1970

Solution B.

	cc.	Barium sulphate.
1.	50	0.3277
2.	50	0.3271
3.	50	0.3279
	Average	0.3275

Solution C.

	cc.	Barium sulphate.
1.	5	0.1944
2.	5	0.1940
	Average	0.1942

Solution D.

	cc.	Barium sulphate.
1.	25	0.1544
2.	25	0.1534
3.	25	0.1543
4.	25	0.1538
5.	25	0.1535
6.	25	0.1546
7.	25	0.1539
	Average	0.1542

Rejecting Nos. 2 and 5.

BARIUM CHLORIDE SOLUTIONS.

Solution A.

	cc.	Barium sulphate.
1.	20	0.1181
2.	20	0.1812
3.	20	0.1811
4.	20	0.1792
5.	20	0.1802
	Average	0.1805

Rejecting No. 4.

Solution B.

	cc.	Barium sulphate.
1.	50	0.1985
2.	50	0.1980
3.	50	0.1086
4.	50	0.1985
	Average	0.1984

Solution C.

	cc.	Barium sulphate.
1.	10	0.4004
2.	10	0.4002
3.	10	0.4006
	Average	0.4004

Solution D.

	cc.	Barium sulphate.
1.	10	0.3998
2.	10	0.3994
3.	10	0.3996
	Average	0.3996

Note.—The apparent discrepancies in some of the above averages are to be explained by the fact that before beginning the work the burette used had been very carefully calibrated, and the averages were calculated to correct number of cubic centimeters from the readings as given on the burette. In the course of the work this refinement was found to be wholly unnecessary and was therefore disregarded.

The equation of solutions of sulphuric acid and of barium chloride is: Twenty cc. barium chloride solution = 21.8 cc. sulphuric acid. That is, when mixed in these proportions they will, theoretically, mutually precipitate each other and give 0.1970 gram barium sulphate.

The effect of bringing these two solutions together in this proportion was first tried. The barium chloride solution plus water to make the whole volume up to 140 cc. was heated to boiling and the sulphuric acid run in from the burette.

		Barium sulphate.	Error.
1.	20 cc. $BaCl_2A$+21.8 cc. H_2SO_4A	0.1966	−0.0004
2.	20 " " " " "	0.1973	+0.0003
3.	20 " " " " "	0.1979	+0.0009

Solutions of $BaCl_2B$ and H_2SO_4, when brought together in their molecular proportions, weighed as follows:

		Barium sulphate.	Error.
1.	50 cc. $BaCl_2B$+ 30.2 cc. H_2SO_4B	0.1979	−0.0005
2.	50 " " " " "	0.1976	−0.0008

These had stood twenty-two hours before filtration, and the results, while not very close, show at least that in water solutions precipitation is practically complete without the presence of an excess of reagent.

A series of precipitations was now made in order to determine the effect of varying quantities of hydrochloric acid upon the precipitation when the two reagents were brought together in their molecular proportions.

The barium chloride solution, water to make the volume up to 140 cc., and the hydrochloric acid were heated to boiling and the sulphuric acid run in cold from the burette.

The same quantities of barium chloride and sulphuric acid were used as above. The time of standing before filtration is

marked over each set. Three precipitations were made with each portion of the hydrochloric acid.

SERIES I.

	1. Five cc. hydrochloric acid. Twenty-five hours. Barium sulphate.	2. Ten cc. hydrochloric acid. Twenty-nine hours. Barium sulphate.	3. Fifteen cc. hydrochloric acid. Thirty-three hours. Barium sulphate.	4. Twenty cc. hydrochloric acid. Forty-four hours. Barium sulphate.
1	0.1908	0.1879	0.1827	0.1875
2	0.1902	0.1870	0.1844	0.1863
3	0.1904	0.1881	0.1838	0.1873

It was thought that after standing twenty-four hours precipitation would be complete and a longer time would have no effect. The results of series No. 4 seem to show differently, however. Accordingly another series was run in which the time of standing was regulated. Otherwise the precipitations were made as above.

These stood twenty-three hours before filtration.

SERIES II.

	1. Five cc. hydrochloric acid. Barium sulphate.	2. Ten cc. hydrochloric acid. Barium sulphate.	3. Fifteen cc. hydrochloric acid. Barium sulphate.
1	0.1902	0.1870	0.1852
2	0.1884	0.1854	0.1849
3	0.1904	0.1846	0.1827

	4. Twenty cc. hydrochloric acid. Barium sulphate.	5. Twenty-five cc. hydrochloric acid. Barium sulphate.	6. Thirty cc. hydrochloric acid. Barium sulphate.
1	0.1832	0.1822	0.1766
2	0.1885	0.1793	0.1833
3	0.1850	0.1789	0.1733

The above results show three things: (1) That less barium sulphate is precipitated in the presence of larger amounts of hydrochloric acid, but this solubility is not proportional to the amount of hydrochloric acid. (2) That the greatest variation of results takes place in the presence of the larger amounts of acid. In other words parallel precipitations don't "check." (3) A much longer time is required to reach the maximum of precipitation in the presence of the larger amounts of hydrochloric acid. See No. 4, Series I.

The effect of a small excess of sulphuric acid was now tried. Three solutions each containing fifty cc. barium chloride *B*, sixty cc. water and twenty cc. hydrochloric acid were heated to boiling and the amounts of sulphuric acid *B*, indicated below, were run in from a burette.

These stood twenty-four hours and weighed as follows:

SERIES III.

		Barium sulphate.	Error.
1.	50 cc. $BaCl_2$ *B* + 31.2 cc. H_2SO_4 *B* = 1 cc. excess	= 0.1839	—0.0145
2.	50 " " + 32.2 " " = 2 " "	= 0.1881	—0.0103
3.	50 " " + 33.2 " " = 3 " "	= 0.1971	—0.0013

The filtrates from the above gave no further precipitate on standing several days.

Another series was run, using five cc. hydrochloric acid instead of twenty cc., but conducted otherwise in the same manner except that they stood from Friday to the following Monday and undoubtedly the maximum of precipitation was reached.

SERIES IV.

		Barium sulphate.	Error.
1.	50 cc. $BaCl_2$ *B* + 31.2 cc. H_2SO_4 *B* = 1 cc. excess	= 0.1951	0.0033
2.	50 " " " + 32.2 " " " = 2 " "	= 0.1963	0.0021
3.	50 " " " + 33.2 " " " = 3 " "	= 0.1964	0.0020

It was now decided to use larger amouuts of sulphuric acid in excess, but in order to hurry matters along, cut down the time of standing before filtration.

In the following series, accordingly, the barium sulphate was filtered off after standing three hours. The whole volume of solution in each case was 150 cc.

SERIES V.

	Barium chloride *B*.	Hydrochloric acid.	Sulphuric acid *B*.	No. of cc. in excess of the theoretical am't for precipitation.	Barium sulphate weighed.	Error.
	cc.	cc.				
1	50	15	35.2	5	0.1458	0.0526
2	50	15	40.2	10	0.1590	0.0394
3	50	15	45.2	15	0.1688	0.0296
4	50	15	50.2	20	0.1762	0.0222

A steady increase following the larger amounts of sulphuric acid is seen, but it is to be noted that 30.2 cc. sulphuric acid in

three hours did not bring down so large a precipitation as 31.2 cc. sulphuric acid did in twenty-four hours though in the presence of a larger portion of hydrochloric acid. See Series III.

In order to get comparative results the various conditions of the precipitation had to be more carefully regulated. The above results show this very plainly.

Accordingly, the following problem was set: How great an excess of sulphuric acid is required to precipitate completely as sulphate, the barium from fifty cc. of barium chloride *B*, in the presence of five cc. hydrochloric acid in one hour, the whole volume of solution, after adding the sulphuric acid, to be 150 cc.?

Instead of adding a certain number of cc. in excess the sulphuric acid was now measured in equivalents, 30.2 cc. the exact amount to precipitate fifty cc. barium chloride was called one equivalent and different multiples of it were taken.

The barium chloride, water, and hydrochloric acid were heated on the water-bath and the sulphuric acid run in cold from the burette.

SERIES VI.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *B*.	Eqivalents sulphuric acid.	Barium sulphate.	Error.
1	50	5	37.8	1.25	0.1564	0.0420
2	50	5	45.3	1.50	0.1624	0.0360
3	50	5	52.8	1.75	0.1784	0.0200
4	50	5	60.4	2.00	0.1857	0.0127
5	50	5	68.9	2.25	0.1842	0.0142

The fact that No. 5 was lower than No. 4 was referred to the lowering of temperature produced by the addition of the sixty-eight cc. cold sulphuric acid.

The following plan was now adopted:

The sulphuric acid was measured out into beakers and also heated on the water-bath. It was then added to the barium chloride solution, the beakers being washed out three times with hot water, using about four or five cc. each time and the washings also added.

SERIES VII. (Continued from above.)

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *B*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
6	50	5	67.9	2.25	0.1931	—0.0053
7	50	5	75.5	2.50	0.1935	—0.0049
8	50	5	83.0	2.75	0.1956	—0.0028
9	50	5	90.5	3.00	0.1963	—0.0021
10	50	5	39.4	4.00	0.1961	—0.0023
11	50	5	49.2	5.00	0.1962	—0.0022

Note.—The last two results were obtained with a stronger sulphuric acid solution, which was run in cold.

A rapid increase is seen with the first additions of sulphuric acid, the difference becoming less as the sulphuric acid increases.

Another peculiarity was also seen in each one of these series. Although the solutions had been well stirred on bringing the reagents together, had settled clear in a few minutes, and the supernatant liquid had remained clear, yet in running through the filter the filtrates soon became cloudy and a copious precipitate of barium sulphate settled out.

This could be due only to the agitation produced by running through the filter. Later an experiment was tried on this point. Fifty cc. of barium chloride solution, 0.0992 barium sulphate + five cc. hydrochloric acid and water to make the total volume up to 150 cc., was heated in a flask and two equivalents of sulphuric acid added. This was then shaken for ten minutes, allowed to settle for fifty minutes, and then the precipitate was filtered off and weighed.

It gave barium sulphate 0.1979, a minus error of 0.0013 as against an error of —0.0127 in Series VI, with two equivalents.

It seems that in the presence of hydrochloric acid unless there is a sufficient amount of sulphuric acid present to effect complete precipitation, a delicate balance is formed which is affected by a difference in time of standing, in temperature, and amount of agitation on stirring. To avoid adding so large a volume of sulphuric acid solution "*C*" was prepared.

Series VIII was now run. Both solutions were heated on the water-bath and brought together as described above. Solution

in each case was stirred one and one-half minutes and allowed to settle one hour.

SERIES VIII.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *C*. cc.	Equivalents sulphuric acid.	Barium sulphate.	Error.
1	50	5	20.4	4	0.1971	—0.0013
2	50	5	25.5	5	0.1978	—0.0006
3	50	5	30.6	6	0.1981	—0.0003
4	50	5	35.7	7	0.1980	—0.0004
5	50	5	40.8	8	0.1984	0.0000
6	50	5	45.9	9	0.1985	+0.0001
7	50	5	51.0	10	0.1984	0.0000
8	50	5	56.1	11	0,1985	+0.0001

At last the proper excess to effect complete precipitation under the conditions described above had been found. Seven or eight times the theoretical amount seems necessary. It is to be noted that the change is extremely slow when near the critical point.

A short series was precipitated and weighed, using other solutions, the equation of which was as follows :

Fifty cc. $BaCl_2$, $x = 1$ cc $\pm$ H_2SO_4 $D = 0.1992$ $BaSO_4$.

SERIES IX.

	Barium chloride *x*. cc.	Hydrochloric acid. cc.	Sulphuric acid *D*. cc.	Equivalents sulphuric acid.	Barium sulphate.	Error.
1	50	5	3	3	0.1957	—0.0035
2	50	5	4	4	0.1992	0.0000
3	50	5	5	5	0.1983	—0.0009
3	50	5	5	5	0.1992	0.0000

In this series the sulphuric acid was run in cold.

The maximum amount of precipitate seems to be reached here with less sulphuric acid than when a more dilute solution was used. The same is true of the precipitations made in the presence of ten cc. hydrochloric acid.

Series X was now run, the precipitations being made in exactly the same manner as those of Series VIII, except that ten cc. of hydrochloric acid was put into the solutions instead of five cc.

SERIES X.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *C*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
1	50	10	30.6	6	0.1964	—0.0020
2	50	10	35.7	7	0.1974	—0.0010
3	50	10	40.8	8	0.1981	—0.0003
4	50	10	45.9	9	0.1982	—0.0002
3	50	10	40.8	8	0.1970	—0.0014
4	50	10	45.9	9	0.1982	—0.0002

In the presence of ten cc. hydrochloric acid then, a somewhat greater excess of sulphuric acid is required than with five cc. hydrochloric acid.

A short series with the stronger solution gave

SERIES XI.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *D*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
1	50	10	5	5	0.1975	—0.0017
2	50	10	6	6	0.1982	—0.0010
3	50	10	7	7	0.1992	0.0000
3	50	10	7	7	0.1991	—0.0001

Series XII. was conducted exactly as Nos. VIII. and X., excepting that fifteen cc. hydrochloric acid was used.

SERIES XII.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *C*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
1	50	15	30.6	6	0.1957	—0.0027
2	50	15	35.7	7	0.1955	—0.0029
3	50	15	40.8	8	0.1965	—0.0019
4	50	15	45.9	9	0.1973	—0.0011
5	50	15	51.0	10	0.1972	—0.0012
6	50	15	56.1	11	0.1984	0.0000
7	50	15	61.2	12	0.1983	—0.0001

The point to be noted in this series is that more sulphuric acid is required in the presence of the larger amount of hydrochloric acid.

The other side of the question was now taken up, namely, the precipitation of sulphuric acid with an excess of barium chloride in the presence of hydrochloric acid.

A new difficulty at once presented itself. The old trouble in filtering barium sulphate was experienced. When a small amount of hydrochloric acid was present it was found utterly impossible to do it under the conditions which had previously been followed.

Various experiments were made to avoid this trouble and at last the following scheme was adopted:

The volume was kept at 150 cc. as in the other work. The sulphuric acid, water, and hydrochloric acid were heated on the water-bath and the barium chloride solution, also hot, was added drop by drop with constant stirring. The beakers were then set back on the bath and the solutions stirred at intervals for thirty minutes. They were then set off and stirred at intervals again until cold.

Just before pouring upon the filter the precipitate was stirred up and the filter filled several times. At first a small portion ran through, but this was poured back, and, generally, the rest could be filtered without trouble.

A series was run according to this description, except that the volume was 250 cc.

The exact time of standing before filtering was not noted in this case. It was probably about four or five hours.

SERIES XIII.

	Sulphuric acid *B*. cc.	Hydrochloric acid. cc.	Barium chloride *C*. cc.	Eqivalents barium chloride.	Barium sulphate.	Error.
1	30.2	10	14.9	3	0.1967	—0.0017
2	30.2	10	19.8	4	0.1959	—0.0025
3	30.2	10	14.9	5	0.1965	—0.0019

There was nothing satisfactory to be derived from this series, so Series XIV was run. The volume here was kept down to 150 cc.

SERIES XIV.

	Sulphuric acid *B*. cc.	Hydrochloric acid. cc.	Barium chloride *C*. cc.	Equivalents barium chloride.	Barium sulphate.	Error.
1	30.2	10	14.9	3	0.1975	—0.0009
2	30.2	10	19.8	4	0.1994	+0.0010
3	30.2	10	24.9	5	0.1983	—0.0001
4	30.2	10	29.8	6	0.2005	+0.0021

Two of these precipitates weigh heavier than theory demands. This could come only from contamination with barium chloride. To test this No's 3 and 4 were transferred to beakers, boiled up with about seventy-five cc. of water and again filtered, ignited, and weighed.

They then gave

3. 0.1980 barium sulphate = —0.0004 error.
4. 0.1987 " " = +0.0003 "

Another series was run in exactly the same manner, except that more care was taken in washing. Each precipitate was washed with boiling water until the filtrate no longer reacted with silver nitrate.

SERIES XV.

	Sulphuric acid *B*. cc.	Hydrochloric acid. cc.	Barium chloride *C*.	Equivalents barium chloride.	Barium sulphate.	Error.
1	30.2	10	9.9	2	0.1965	—0.0019
2	30.2	10	14.9	3	0.1982	—0.0001
3	30.2	10	19.8	4	0.1975	—0.0008
4	30.2	10	24.9	5	0.1988	+0.0004
5	30.2	10	29.8	6	0.1994	+0.0010

No's 4 and 5, on being boiled up with water and reweighed, gave

3. 0.1981 = —0.0003 error.
4. 0.1975 = —0.0009 "

At its best, however, this method of working was unsatisfactory. The precipitate seemed always on the point of running through the filter and indeed traces generally did go through.

The following scheme was accordingly tried in Series XVI.

The volume was kept as before at 150 cc., but thirty cc. of hydrochloric acid instead of ten was put into each solution. The precipitates were not stirred up after being thrown down. In presence of this large excess of acid the precipitates soon became coarse and crystalline and settled rapidly. *No trouble whatever was experienced in filtering them.*

SERIES XVI. (These had stood about four hours.)

	Sulphuric acid *E*. cc.	Hydrochloric acid. cc.	Barium chloride *C*.	Equivalents barium chloride.	Barium sulphate.	Error.
1	20	30	4.6	1.5	0.0947	—0.0289
2	20	30	6.2	2.0	0.0997	—0.0239
3	20	30	9.3	3.0	0.1114	—0.0122
4	20	30	12.4	4.0	0.1169	—0.0067
5	20	30	15.5	5.0	0.1207	—0.0029
6	20	30	18.6	6.0	0.1192	—0.0044

These filtrates, on standing over night, all showed further precipitates of barium sulphate. The series was accordingly continued, this time the solutions standing about seven hours before being filtered.

The precipitates were crystalline and filtered easily and rapidly and the filtrates, on further standing, showed no traces of barium sulphate.

In spite, however, of the greatest care in washing, it was impossible to get rid of the occluded barium chloride before ignition.

SERIES VII.

	Sulphuric acid *E*.	Hydrochloric acid.	Barium chloride *C*.	Equivl's Barium chloride.	Barium sulphate.	Error.
1	20	30	18.6	6	0.1258	+0.0022
2	20	30	21.7	7	0.1252	+0.0016
3	20	30	24.8	8	0.1268	+0.0032
4	20	30	27.9	9	0.1260	+0.0024

Nos. 2, 3 and 4 were boiled up with water, rewashed, ignited and weighed.

	Barium sulphate.	Error.	
2	0.1236	0.0000	Filtrate reacted strongly with silver nitrate.
3	0.1238	+0.0002	" " " " " "
4	0.1253	+0.0017	" " slightly " " "

No. 4 boiled up the second time 0.1237 $BaSO_4 = + 0.0001$ error. The filtrate in this case reacted strongly with silver nitrate.

To test this boiling up process No. 4 was treated the third time. This time the precipitate weighed 0.1235 and the filtrate did *not* react with silver nitrate.

A last experiment was made to determine the effect of barium

chloride upon the direct solubility of barium sulphate in hydrochloric acid.

0.1248 gram barium sulphate was put in 120 cc. water and thirty cc. hydrochloric acid and beaker marked "*A*."

0.1228 gram barium sulphate was weighed into another beaker with 105 cc. water, thirty cc. hydrochloric acid and fifteen cc. barium chloride *C*. This beaker was marked "*B*."

Both were heated on the water-bath with frequent stirring and then stood over night.

On being filtered and weighed,

"*A*" gave	—0.1106	barium sulphate	= 0.0142	loss.
"*B*" "	—0.1228	" "	= 0.000	"

To further test precipitate "*B*" it was boiled up with water as those of Series XVII, and re-weighed. It lost by this operation 0.0002, which is practically nothing.

From the results obtained in this investigation the following conclusions seem justified:

(1) In the precipitation of a barium salt with sulphuric acid in the presence of hydrochloric acid, a very large excess of sulphuric acid is required.

(2) This excess should be greater the greater the amount of hydrochloric acid present in the solution.

(3) It should be greater the shorter the time of standing before filtration. In fact a very great excess seems to effect immediate precipitation.[1]

(4) The greater the excess of sulphuric acid the less stirring seems necessary to bring down the precipitate in a given time.

(5) While barium sulphate obtained by precipitating a barium salt with sulphuric acid in the presence of hydrochloric acid is coarse, crystalline and easily filtered,[1] that obtained by precipitating sulphuric acid with a barium salt in the presence of hydrochloric acid is fine and much disposed to run through the filter unless special precautions are taken.

(6) In general a large excess of barium chloride is required to completely precipitate the sulphuric acid in the presence of hydrochloric acid.

[1] *J. Anal. Appl. Chem.*, 5, 278.

(7) As the hydrochloric acid increases the amount of barium chloride should also be increased.

(8) The greater the amount of hydrochloric acid present the coarser and more crystalline in character is the precipitated barium sulphate. In precipitating in the presence of large amounts of hydrochloric acid the solution should be quite concentrated.

(9) The barium sulphate so obtained, will, however, be contaminated with adhering barium chloride, and no amount of washing before ignition can entirely free it from this occluded chloride. If, after ignition, the precipitate be boiled up with water, again washed, ignited and weighed, and this process be continued until a constant weight is obtained, the sulphate may be entirely freed from the barium salt.

Some subsequent work in this line has shown that heavy precipitates sometimes require three or four treatments before a constant weight is obtained.

(10) Both in the precipitation of barium with sulphuric acid and of sulphuric acid with barium, very concordant results may be obtained if the conditions under which the precipitations are made are similar, but these results may be quite far from correct. A note of this commonplace occurrence in analytical work is made here, because by following the usual method of testing the filtrate for an excess of the precipitating reagent, a strong reaction might be obtained and yet not more than ninety per cent. of the original precipitate be down.

In conclusion I wish to express my thanks to Professor N. W. Lord for helpful suggestions during the course of this work.

DISCUSSION.[1]—T. S. Gladding: I have already shown (see this Journal, **16**, 398; **17**, 181, 397, 772; **18**, 446) that correct results may be obtained if the barium chloride solution be added drop by drop instead of all at once. This is confirmed by Lane (**18**, 682) and is now virtually admitted by Lunge, who precipitates (**18**, 686) by "quick additions (*i. e.*, pouring in the hot barium chloride solution in about ten portions, occupying about half a minute in all, and stirring the mixture all the time, as every chemist would do.)"

[1] Buffalo Meeting, Aug., 1896.

THE ACTUAL ACCURACY OF CHEMICAL ANALYSIS.[1]

BY FREDERIC P. DEWEY.

Received July 14, 1896.

THE subject of this paper does not embrace the consideration of ways and means for the increase of analytical accuracy, or the question, what can be or should be attained in that direction. I desire simply to call attention to the degree of accuracy exhibited in actual every day practice. In estimating this, little weight will be given to the evidence afforded by the agreement of duplicate or multiple determinations by the same chemist; for I am convinced that such agreement is a delusion and a snare. Nor will special importance be attached to the agreement of two or even three analysts in special cases, or to the agreement between two methods practiced by the same analyst. I propose to compare the results obtained by several chemists, working upon the same sample and by various methods, in order to exhibit, as I have said, the actual condition of practice.

The available material for illustrating this phase of the question is unfortunately scanty; but something has been done; and I hope, by calling attention to some of the work in this line, to stimulate further work in the same direction by inducing others to prepare suitable samples and submit them to various chemists who are competent and willing to make the necessary determinations and fully describe the methods they employ.

I draw most of my illustrations from the "Transactions of the American Institute of Mining Engineers," the "Proceedings of the Association of Official Agricultural Chemists," and from personal experience.

MANGANESE IN STEEL.

In May, 1881, Mr. William Kent presented a paper to the American Institute of Mining Engineers entitled "Manganese Determinations in Steel,"[2] in which he gave twenty-four determinations of manganese, made by ten different chemists, employing two main methods, on samples from a plate of steel.

[1] Read before the Washington Section of the American Chemical Society, May 14th, 1896, and published jointly with the American Institute of Mining Engineers.

[2] Trans. A. I. M. E., 10, 101.

These results presented the remarkable range of from 1.14 to 0.303 per cent., and one chemist reported results ranging from 1.14 to 0.434 per cent.

A portion of this variation was undoubtedly due to variations in the sample, since the same sample was not used throughout by the different chemists.

Throwing out the anomalous result of 1.14 per cent. we have twenty-three determinations running from 0.619 per cent. to 0.303 per cent., with an average of 0.415 per cent. Thus showing that at that time the determination of manganese in steel, when only about four-tenths per cent. was probably present, might exhibit an extreme variation between the highest and the lowest results of about three-tenths per cent., or seventy-five per cent. of the amount of manganese present.

These results were certainly very discouraging; but if they did nothing else they served to call attention to the very unsatisfactory character of the determination of manganese in steel at that time.

I do not recall any recent symposium on the determination of manganese in this class of material, but in 1886 Capt. A. E. Hunt,[1] in giving a measure of the accuracy of the colorimetric method, speaks of a variation of 0.02 per cent. in steels containing 0.15 to one and five-tenths per cent. of manganese as "sufficiently accurate for all practical work," thus clearly intimating that the current results of analysis by other methods were at least as good. This degree of accuracy, if attained by different chemists upon the same sample, must be considered a satisfactory advance over the results reported by Mr. Kent.

Early in 1883 Mr. G. C. Stone began a series of contributions on the "Determination of Manganese in Spiegel."[2] In his first paper he reported thirteen determinations by five chemists, all working upon the same "works" sample, showing from 15.49 to 13.83 per cent., and also twenty-six determinations by ten chemists, all working upon a sample of the same spiegel, prepared with especial care jointly by Mr. Stone and one of the other chemists, showing from 14.56 to 10.36 per cent. But some of the low results were obtained by experimental methods.

[1] Trans. A. I. M. E., 15, 104.

[2] Trans. A. I. M. E., 11, 323: 12, 295 and 514.

In the fall of 1883 Mr. Stone reported twenty additional determinations by five other chemists, ranging from 14.20 to 10.76 per cent.; the extremes being reported by the same chemist when working by different methods, his favorite method giving from 13.84 to 13.65 per cent., and three low results, less than eleven per cent., being obtained by the Williams' method. In this connection Mr. Stone presented an interesting table, dividing the methods used into four classes and the results into three classes, giving respectively, below thirteen per cent., between thirteen and fourteen per cent., and above fourteen per cent.

In the spring of 1884 Mr. Stone reported twenty-seven new results, nineteen by four new chemists, and eight by one previously reported, whose new results were obtained by several methods.

We have thus seventy-three determinations by nineteen different chemists. Of these two are thrown out on account of the method used, and eleven "because the chemists were not entirely satisfied with them," leaving sixty determinations by eighteen chemists, using twelve methods.

These sixty results range from 14.47 to 12.60 per cent., and average 13.39 per cent. Leaving out eight determinations by one method which is considered to give low results, the lowest determination becomes 12.92 per cent. and the average 13.48 per cent., showing an extreme variation of 1.45 per cent. of manganese between the highest and lowest results, and showing only forty-four per cent. of the results within two-tenths per cent. of the average.

In the discussion of Mr. Stone's second paper, Mr. J. B. Mackintosh[1] presented an analysis of Mr. Stone's first forty-six results, retaining the results by the Williams' method, from which he argued that the evidence pointed to 12.956 per cent. as the true content of manganese in this spiegel. If this is the case, then there is a very decided tendency to get too high results in this class of work.

Taken as a whole, this investigation would seem to show that variations of five-tenths per cent. in the determination of manganese in this grade (ten to fifteen per cent. manganese) of

[1] Trans. A. I. M. E., 12, 300.

spiegel are to be expected, and much wider variations may be found.

PHOSPHORUS IN PIG IRON.

Early in the 80's, Messrs. Potter and Riggs, of St. Louis, Mo., sent out a sample of pig-iron for the determination of phosphorus.

This examination yielded twenty-six results, by eleven chemists, using five methods, ranging from 0.181 to 0.141 per cent., and averaging 0.160 per cent. and showing an extreme variation of 0.040 per cent. The maximum variation reported by any one chemist was 0.017 per cent., while three reported duplicates agreeing with 0.001 per cent. These results have never been published. One of the chemists discovered arsenic in the sample, which would account for some of the variation in the series. His determinations in duplicate were 0.151 and 0.152 per cent.

In February, 1882, Mr. F. E. Bachman presented a paper to the American Institute of Mining Engineers,[1] in which he reported forty-four results by eighteen chemists, using four methods, ranging from 0.165 to 0.096 per cent. and averaging 0.143 per cent. The extreme variation was 0.069 per cent. The maximum variation reported by any one chemist on straight duplicates was 0.01 per cent., and the minimum 0.0004 per cent. Experimental determinations by Mr. Bachman, using different processes, yielded variations amounting to 0.043 per cent.

At the Atlanta meeting in October, 1895, Mr. Geo. Thackray presented a paper, entitled "A Comparison of Recent Phosphorus Determinations in Steel."[2] He first gives a table of determinations of phosphorus by two chemists on eight samples ranging from 0.033 to 0.012 per cent., one chemist uniformly getting high results. One chemist found from 0.080 to 0.074 per cent., and the other 0.110 to 0.088 per cent in these steels. These results were manifestly unsatisfactory.

A second table shows results by three chemists, the buyer's, the seller's and an arbitrator. By the arbitrator's determinations these steels carried from 0.080 to 0.063 per cent. of phosphorus.

1 Trans. A. I. M. E., 10, 322.
2 Trans. A. I. M. E., 25, 370.

The maximum difference in any set of three results was 0.017 per cent., and the minimum 0.005 per cent.

These results were obtained in the settlement of sales. As a result of the discussion which accompanied the matter, two samples of steel were prepared and sent to various chemists. A fourth table gives thirty-six results obtained from twenty-three chemists, using twenty-nine methods on one steel, showing results averaging 0.0496 per cent., and ranging from 0.055 to 0.045 per cent., an extreme variation of only 0.010 per cent. Any individual result was practically within 0.005 per cent. of the average.

On the second sample thirty-eight results were reported averaging 0.0835 per cent., and ranging from 0.091 to 0.076 per cent., an extreme variation of 0.015 per cent.

My own results on these steels are not given, as they were not reported in time; but they add two more results by one more chemist in each case, and the results fall within the limits.

These results must be regarded as highly satisfactory, and show that here, at least, is one determination that can be made by many chemists, working in different ways, and yet with results agreeing very closely together. While it may not be necessary to determine many things as closely as phosphorus in steel, yet it would be highly satisfactory if we could do so; and this is a good standard of excellence for us to aim at.

PHOSPHORIC ACID.

As compared with the accuracy secured in the determination of phosphorus in steel, the 1894 report of the Association of Official Agricultural Chemists,[1] shows that on one sample thirty-nine determinations of insoluble phosphoric acid by eighteen chemists, working by the official method, showed results ranging from 0.45 to 0.03 per cent., with an average of 0.27 per cent., the extreme variation being 0.42 per cent., or over one and one-half times the average determination.

By another method, on the same sample, thirty-six determinations by nineteen chemists showed results varying from 0.34 to

[1] Proceedings of the Eleventh Annual Convention of the Association of Official Agricultural Chemists, August 23, 24, 25, 1894. Bulletin 43, U. S. Department of Agriculture, Division of Chemistry, p. 76.

0.04 per cent., with an average of 0.19 per cent., the extreme variation being 0.30 per cent., or over one and one-half times the average.

We have thus seventy-five determinations by nineteen chemists working by two methods, showing results ranging from 0.45 to 0.03 per cent., with an average of 0.233 per cent., the extreme variation being 0.42 per cent., or nearly twice the average determination.

On another sample thirty-three determinations by seventeen chemists working by the official method, showed results ranging from 3.85 to 2.24 per cent., with an average of 2.82 per cent., the extreme variation being 1.61 per cent., or considerably more than one-half of the average.

By another method, on the same sample, thirty-five determinations by seventeen chemists showed results ranging from 3.49 to 2.18 per cent., with an average of 2.83 per cent., the extreme variation being 1.31 per cent., or nearly one-half the average.

Summing up again, we have sixty-eight determinations by eighteen chemists working by two methods, showing results ranging from 3.85 to 2.18 per cent., with an average of 2.82 per cent., the extreme variation being 1.67 per cent.

The same report[1] shows that on one sample the results of twenty-nine determinations of citrate soluble phosphoric acid by fourteen chemists, by the direct method of Ross, varied from 2.47 to 1.04 per cent., with an average of 1.52 per cent., the extreme variation being 1.43 per cent., or nearly equal to the average of all the determinations.

On the same sample, by the official method, the results of twenty-three determinations by fourteen chemists ranged from 2.26 to 1.18 per cent., with an average of 1.46 per cent., the extreme variation being 1.08 per cent., or over two-thirds of the average determination.

Summing up, we have fifty-two determinations by fourteen chemists working by two methods, ranging from 2.47 to 1.04 per cent., and averaging 1.49 per cent., the extreme variation being 1.43 per cent., or nearly equal to the average.

[1] *Ibid.*, p. 72.

On another sample thirty-six determinations by fifteen chemists by the direct method of Ross, range from 3.29 to 1.87 per cent., with an average of 2.36 per cent., the extreme variation being 1.42 per cent., or considerably over one-half of the average determination.

On the same sample, twenty-four determinations by fifteen chemists, ranged from 3.40 to 2.08 per cent., with an average of 2.60 per cent., the extreme variation being 1.32 per cent., or a little over one-half of the average determination.

Summing up, we have sixty determinations by fifteen chemists working by two methods, ranging from 3.40 to 2.08 per cent., and averaging 2.44 per cent., the extreme variation being 1.32 per cent., or a little over one-half of the average determinations.

In the determination of the total phosphoric acid,[1] forty-five determinations, by eighteen chemists, ranged from 20.67 to 19.74 per cent., with an average of 20.09 per cent., the extreme variation being 0.93 per cent. By a volumetric method, thirty determinations, by eleven chemists, ranged from 20.60 to 19.83 per cent., with an average of 20.14 per cent., the extreme variation being 0.77 per cent. By another volumetric method, twenty-one determinations by ten chemists, ranged from 20.45 to 19.27 per cent., with an average of 19.96 per cent., the extreme variation being 1.18 per cent.

Combining these results, we have ninety-six determinations by eighteen chemists working by three methods, ranging from 20.67 to 19.27 per cent., with an average of 20.08 per cent., the extreme variation being 1.40 per cent.

Similarly, on another sample, we have 120 determinations, by twenty-two chemists, working by the same three methods, ranging from 18.15 to 16.25 per cent., with an average of 17.26 per cent., the extreme variation being 1.90.

Again, on another sample, we have ninety-six determinations by twenty-one chemists, working by the same three methods, ranging from 2.85 to 2.20 per cent., with an average of 2.50 per cent., the extreme variation being 0.65 per cent.

COPPER.

At the August meeting of the A. I. M. E., in 1882, Mr. W.

[1] *Ibid.*, pp. 81, 82, 83.

E. C. Eustis presented a paper entitled "Comparison of Various Methods of Copper Analysis."[1] For the purpose of this comparison a very complex sample was made up, containing sulphides, oxides and metallic copper, a silicate, sulphides of iron and zinc, arsenic and nickel. The paper reports forty-five determinations by seventeen chemists, using some eight methods. The results showed a wide variation, ranging from 53.34 to 43.92 per cent. and averaging 47.75 per cent. On throwing out a set of six results from one concern, all of which were more than two per cent. and two of them nearly five per cent. above the nearest other result, as being manifestly too high, and two results by one chemist and one method, which were more than two per cent. below the nearest other result, the series still ranges from 48.72 to 46.24 per cent., with an average of 47.23 per cent., and a maximum variation of 2.48 per cent., which cannot be considered very satisfactory.

The same paper reported seventeen determinations by seven chemists on borings of pig copper. These ranged from 91.07 to 98.17 per cent. and averaged 94.25 per cent. On throwing out two results that were nearly three per cent. higher than the nearest other result, and four that were over three per cent. below the nearest other result, the series ranges from 94.91 to 94.38 per cent. with an average of 94.69 per cent. The extreme variation of only 0.53 per cent. must be regarded as very good work, especially when we consider the character of the material.

At the Florida meeting in March, 1895, the results of a symposium on copper and copper matte, initiated by Dr. A. R. Ledoux, of New York City, were presented.[2] Eight chemists reported the copper in the matte, some in duplicate or more, as determined by electrolysis, as ranging from 55.17 to 54.50 per cent. and averaging 54.91 per cent. The extreme variation was only 0.67 per cent; and this must be regarded as satisfactory, and very much better than the results on Mr. Eustis' complex mixture.

Six chemists reported results by the cyanide method, ranging from 54.8 to 50.55 per cent, all but one of the results being below

[1] Trans. A. I. M. E., 11, 120.
[2] Trans. A. I. M. E., 25, 250 and 1000.

the lowest electrolytic result. These cannot be regarded as satisfactory.

A plate of copper made from melted anodes was drilled and six chemists reported the copper in the drillings, as found by the electrolytic method, as ranging from 98.46 to 97.04 per cent., and averaging 97.67 per cent. with a maximum difference of 1.42 per cent. These results are not as good as those previously reported by Mr. Eustis.

GOLD AND SILVER IN COPPER MATERIALS.

The symposium above referred to was undertaken primarily to test methods of assaying copper material for gold and silver. Fourteen chemists reported the silver by scorification assay, some entirely uncorrected, some partially corrected, and some corrected for both loss in slag and cupel and presence of copper in the silver button. The averaged results ranged from 135.38 to 122.88 ounces per ton and averaged 128.86 ounces per ton; the extreme variation being 12.5 ounces per ton, or nine and seven-tenths per cent. of the average.

Nine chemists reported ten results by combined wet and scorification methods, a few of them corrected for slag and cupel absorption. The averaged results ranged from 130.68 to 123.03 and averaged 127.25 ounces per ton. The extreme variation was seven and six-tenths ounces per ton, or 5.97 per cent. of the average determination.

One chemist reported 123.6 ounces per ton by crucible method.

Another reported 126.2 ounces per ton by combined wet and crucible method, corrected for slag and cupel.

Summing up, we have twenty-six results by twenty chemists working by two main methods, but both of them modified in various ways, and two methods, each by a single chemist, varying from 135.38 to 122.88 and averaging 127.94 ounces per ton. The extreme variation was 12.5 ounces per ton, or 9.77 per cent. of the average determination.

In the case of the silver assay of the copper borings, nine chemists reported by the scorification method, with and without corrections. The averaged results varied from 164.35 to 154.40, and averaged 159.36 ounces per ton. The extreme variation was 9.95 ounces per ton, or 6.24 per cent. of the average.

Fifteen chemists reported sixteen results by combined wet and scorification methods, with and without corrections. The averaged results varied from 161.40 to 148.50 and averaged 156.48 ounces per ton. The extreme variation was 13.9 ounces per ton, or 8.88 per cent. of the average. A single chemist reported 161.35 ounces per ton by combined wet and crucible process, corrected for slag and cupel.

Summing up, we have twenty-six determinations by twenty chemists working by three methods, ranging from 164.35 to 148.5 and averaging 157.67 ounces per ton. The extreme variation was 15.85 ounces per ton, or 10.05 per cent. of the average determination.

Twenty chemists working by the four methods reported twenty-six results on the gold in the matte varying from 2.41 to 1.85 and averaging 2.245 ounces per ton. The extreme variation was 0.56 ounce per ton, or 24.94 per cent. of the average.

On the gold in the copper borings twenty chemists working by two main methods, each one variously modified, and the combined wet and crucible method by a single chemist, reported twenty-six results varying from 0.501 to 0.205 and averaging 0.307 ounce per ton. The extreme variation was 0.296 ounce per ton, or 96.4 per cent. of the average determination.

POTASH.

In the determination of potash the 1894 report of the Association of Official Agricultural Chemists[1] gives six determinations of potassium chloride by six chemists by one method, ranging from 97.79 to 99.32 per cent. with an average of 98.56 per cent, the extreme variation being 1.53 per cent. By another method on the same sample seven determinations by seven chemists range from 97.21 to 98.86 per cent., averaging 98.16 per cent. Combining these results we have thirteen results by seven chemists, by two methods, ranging from 97.21 to 99.32 per cent. and averaging 98.35 per cent., the extreme variation being 2.11 per cent.

This report contains also a table of results on soil analyses[2] which I quote entire.

1 page 22.
2 page 41.

TABLE OF AVERAGES.

Soil Sample No. 2.

	Provisional method.					Hilgard method.				
	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.
		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.	
Insoluble matter	14	76·874	77·733	76·19	2	12	76·619	77·910	75·380	3·3
K_2O	13	0·405	0·510	0·27	59	11	0·431	0·670	0·250	98
CaO	13	0·460	0·605	0·360	53	10	0·538	0·680	0·390	54
MgO	11	0·425	0·589	0·360	54	9	0·425	0·627	0·320	72
Fe_2O_3	9	3·504	4·260	2·955	37	7	4·347	6·400	3·300	70
Al_2O_3	9	6·613	7·500	6·240	19	7	6·285	6·828	4·460	38
P_2O_5	16	0·496	0·600	0·410	38	12	0·510	0·660	0·430	45
Fe_2O_3, Al_2O_3, and P_2O_5	12	10·754	11·400	10·220	11	10	11·071	12·100	10·550	14
N	7	0·276	0·290	0·262	10	..	.....	.....	.....	....
P_2O_5, Goss method	5	0·467	0·493	0·425	15	..	.....	.....	.....	....

Soil Sample No. 3.

	Provisional method.					Hilgard method.				
	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.
		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.	
Insoluble matter	11	80·520	81·255	79·980	1.6	10	80·448	82·010	79·47	3·1
K_2O	10	0·422	0·500	0·305	46	9	0·396	0·630	0·240	98
CaO	9	0·372	0·425	0·300	33	8	0·411	0·600	0·275	79
MgO	8	0·381	0·524	0·270	67	7	0·369	0·490	0·265	61
Fe_2O_3	6	3·251	4·330	2·310	62	5	3·746	4·870	3·025	49
Al_2O_3	6	6·191	7·440	5·670	29	5	5·770	6·164	5·050	19
P_2O_5	11	0·418	0·555	0·350	49	9	0·429	0·560	0·309	59
Fe_2O_3, Al_2O_3, and P_2O_5	8	9·927	10·350	9·440	9	7	10·091	10·590	9·550	10
N	6	0·190	0·224	0·175	26	..	.....	.....	.....	....
P_2O_5, Goss method	4	0·369	0·390	0·354	10	..	.....	.....	.....	....

REVIEW.

ON THE DEVELOPMENT OF SMOKELESS POWDER.[1]

By Charles E. Munroe.

To intelligently present a sketch of what has been done in the development of smokeless powder, it is necessary to first briefly review the history of black gunpowder. Although the place and date of its origin and the name of its inventor are yet open to dispute, it is generally accepted that it was employed as a propellent in cannon at the battle of Crécy in 1346, and in small arms for some time prior to this date, and that it then consisted of a mixture of niter, charcoal and sulphur. Considering the existing state of chemistry, it is fair to infer that the making of gunpowder, like the manufacture of guns, was for long an empiric art, and that, notwithstanding that Tartaglia, Galileo, Newton, Huygens, and many others speculated upon and discussed the effects which gunpowder produced upon projectiles; that granulating was employed in 1445; that Cellini had observed the necessity of adapting the grains to the piece; that sizing was practised in France in 1525, and that Hawksbee had in 1702 measured the volume of gas resulting from a known volume of gunpowder, the science of gunnery had no existence until Robins devised the ballistic pendulum by which he measured the velocity of projectiles and with which he obtained the experimental data upon which his "New Principles of Gunnery," printed in 1742, was founded. The science of exterior ballistic was materially improved when Hutton, in 1778, extended Robins' principle to the use of the gun as the pendulum also, for it became then possible to not only measure the velocity of the projectile, but the energy involved in the reaction, and this method was employed for larger and larger calibers until it reached its practical limit in the very elaborate and precise series of experiments made at the arsenal in this city (Washington) from 1842 to 1847, by Major Mordecai, who succeeded in swinging cannon weighing about 7,700 pounds and throwing 32-pound balls; but this necessitated the use of a pendulum weighing over 9,300 pounds, the center of gravity of which was over fourteen feet below the axis of suspension. The weight and length of the pendulum increases so rapidly with the increase of the projectile that to determine by this method the velocity of the projectile from a 100-ton gun, would require towers like those from which the Brooklyn bridge is suspended, between which to swing the pendulum.

[1] Presidential addrees delivered before the Washington Section of the American Chemical Society, Feb. 21, 1896.

Opportunely as this limit was approached, Dr. Joseph Henry announced, in 1843, his invention of a method for the determination of velocities by interposing screens, which were electrically connected with chronographs, in the path of a projectile and at definitely determined distances from the gun, and this method, which while possessing the merit of great simplicity, is at the same time very precise and capable of being used for determining the velocities of projectiles from guns of every calibre, is now universally employed with chronographs, such as the Boulengé, Schultz-Deprez, and Mahieu, while the principle has been extended by Captain Noble to the study of interior ballistics, in his very ingenious chronoscope by which the velocity of the projectile can be determined at frequent intervals, even when it is moving through the bore of the gun.

The ability to measure the velocities which it produced led to active investigations into the properties of gunpowder and resulted in the experiments of Lavoisier, between 1777 and 1778 on the deflagration of powder, of Berthollet, on the best proportions for mixing the ingredients, of Gay Lussac, on the refining of niter, of Violette, on the production, composition and properties of charcoal, of Gay Lussac and Chevreul, of Bunsen and Schischkoff, of Linck, and of Károyli, on the composition and volume of the products of the combustion of this substance, and of many other experimenters on the effects resulting from differences in the density, hardness, size of grain and other physical characteristics of the explosive. But notwithstanding the great advance made through the invention of methods by which to measure the velocity of the projectile and the recoil of the piece, the science of gunnery was still incomplete without an accurate knowledge of what was going on within the chamber and particularly what pressures were produced and how this pressure was distributed within the gun before the projectile left its seat and while it was traveling through the chase; yet, although direct experimental determinations of the pressure exerted by fired gunpowder were made by Count Rumford in 1797 in a somewhat rude device, and numerous indirect estimations were deduced from the observations of Robins on the volume of the gases produced by its combustion and from the more precise and detailed researches of Bunsen and Schischkoff and the other experimenters previously referred to, no practical means were at command by which to make direct measurements of the pressure developed within the gun itself until Captain Rodman, in 1857, invented the pressure gauge, described in his "Reports of Experiments," published in Boston, in 1861, which in common with several modifications of it, such as the Noble

crusher gauge and the Woodbridge spiral gauge, came into general use in all experimental firing and in the proving of guns and powders.

In estimating the pressure developed by powder from the data obtained in their chemical analyses of its products, Bunsen and Schischkoff proceeded on the assumption that Piobert's conclusion from his experiments, *viz.*, "that the rate of combustion of powder is not affected to any sensible degree by heat or pressure," was correct; but their conclusions having been questioned by many authorities, among them by Vignotti, in 1861, and by Craig about the same time, who showed that the products of combustion differs with the pressure, and their physical data by F. A. P. Barnard, who submitted them to a reinvestigation in 1863, and arrived at a widely different result; and they having also failed of verification by the pressure gauge, the matter was again experimentally attacked by Noble and Abel, who employed as a firing chamber a hermetically closed steel cylinder sufficiently strong to resist rupture by the explosion of a charge of powder which completely filled it (such as Dr. Woodbridge had previously used at the Washington navy yard in 1856), in which pressure gauges were enclosed, and they fired the charge by the electric method invented by Dr. Robert Hare in 1832. In addition the apparatus was so contrived that the gaseous and solid products could be collected, measured and analyzed at will.

With this they found that when powder is fired in a confined space the products of combustion are about fifty-seven per cent. by weight of ultimately solid matter, and forty-three of gases, which at 0° C. and 760 mm., occupy about 280 times the volume of the original powder. That the temperature of explosion is about 2,200° C., and the tension of the products, when the powder entirely fills the space in which it is fired, is about 6,400 atmospheres, or forty-two tons per square inch.

When fired in the bore of the gun it was shown that the work on the projectile is effected by the elastic force resident in the permanent gases, but the reduction of temperature, due to the expansion of the permanent gases, is in a great measure compensated for by the heat stored up in the liquid residue. The total theoretical work of gunpowder when expanded indefinitely (as for instance in a gun of infinite length) was deduced from the data which they accumulated as about 486 foot tons per pound of powder.

They further ascertained that the fine grain powders furnish decidedly smaller portions of gaseous products than large grain or cannon powders; that the variations in the composition of

the products of explosion, in a closed vessel, furnished by one and the same powder, under different conditions as regards pressure, and by two powders of similar composition, under the same conditions of pressure, are so considerable that no chemical expression can be given for the metamorphosis of a gunpowder of a normal composition, and that the proportions of the several constituents of the solid residue are quite as much affected by slight accidental conditions of explosion of one and the same powder in different experiments as by decided differences in the composition or in the size of the grain.

The subsequent researches of Berthelot and Vieille, and of Sarrau and Vieille showed that gunpowder was not singular in that its combustion products varied with the variations in the conditions prevailing in the firing chamber, but that this same rule held for gun cotton, picrates and other explosives, also, and that consequently the chemical reaction taking place and the physical phenomena attending them were changed with these varying conditions, and more particularly with variations in the density of loading.

Before the invention of the instruments of precision above alluded to, guns were constructed largely on principles deduced from observations of exterior phenomena, and powder was manufactured largely by rule of thumb. With the ability to determine quantitatively their behavior, each has been studied in a scientific manner and improved by rational methods.

By their use the real importance of uniformity in chemical and physical composition was demonstrated for the powder, and the means by which to "prove powder" before issue were supplied, while rational blending, by which to minimize the irregularities incident to the best commercial processes was made possible. At the same time greater uniformity in granulation was secured; the best form of grain was developed for great guns through the pebble to the mammoth, disk, pellet, sphere, cylinder, hollow cylinder, hexagon and cube to the hexagonal prism, with one canal, which is now generally adopted, and which is a modified form of the grain invented by Rodman; the size of the grain best adapted for a given gun was ascertained, and the size rose trom one-sixth of an inch, as used in the 15-inch S. B., to fhe hexagonal prism one inch in height by 1.36 inches in diameter; the density of the grain rose from 1.60 to 1.86; the effect of prearranged variations of density in grains, as proposed by Doremus and carried out in the Fossano powder, was determined; and the important part which moisture played in the reactions going on in the chamber with the necessity for introducing it into the grain in definite quantities and retaining it there

within very narrow limits was discovered. In fact these methods of inspection have become so precise and the powder specifications so severe that the manufacture of military gunpowder is now a most difficult art, and the maker must not only watch the barometer and thermometer and hygrometer to determine his action at each step of his process, but according to one authority, he must "vary his treatment with each passing cloud," and notwithstanding all precautions, it is no uncommon thing for the best makers to have their product rejected at the proving ground.

Besides these improvements in black gunpowder, which have resulted from our ability to accurately gauge its performance, these instruments have shown us that it is possible to avail ourselves of the energy stored up in underburned charcoal or carbohydrates if we but modify the brusqueness incident to mixtures containing them by adopting the proper size, form, hardness and density for the grain, and this has resulted in the cocoa or brown prismatic powders which have come into very extented use since 1880.

The valuable properties of the compressed powder were then applied for use in small calibers and enabled Hebler to realize a marked increase in efficiency for his rifles, and in these forms the limit of efficiency of gunpowder appeared to be reached.

But while this was being accomplished, progress was being rapidly made along other lines which we will briefly point out.

Among the other inventions in gunnery which preceded the invention of smokeless powder, and made its use possible or essential, we may mention the introduction of rifling, by which greater accuracy of fire and a higher velocity and penetrating effect is obtained, and which, while invented by Gaspard Zollner, of Vienna, in 1480, did not come into vogue until 1830, or general use until much later. Breech loading, which was known among the Chinese as early as 1313, but which has practically been developed since 1863, our civil war having been fought chiefly with muzzle loaders. Percussion caps, invented by Joseph Egg, in 1818, and adopted, with the nipple, in France in 1838. Self obturating metallic ammunition, which depended on the preceding invention, and which we owe apparently to Flobert, who introduced it for use, with a quick powder, in his parlor rifle in 1845, though it did not come into use for larger caliber for some years later, and then only after the discovery of a metal having the necessary ductility and strength from which to strike the shells and the perfecting of machinery for their economic and rapid production. Magazine rifles and machine guns, the earlier practical forms of the latter being the weapon

exhibited by Dr. Gatling in 1867, and the French mitrailleuse, and which have now developed into the automatic machine guns, such as Maxim, Colt, Hotchkiss, and others possessing an almost incredible rapidity of discharge. Rapid fire large caliber guns, which, like the foregoing, depend for their development on the prior invention of the breech mechanism, and the metallic ammunition and which have reached calibers of six-inch diameter and throw 100-pound shot at the rate of six per minute, with a velocity of over 2,000 feet per second. Breech-loading, built-up steel rifles, which, while embodying the ideas of a gun of equal strength, as announced by Professor Treadwell, in 1843, the mechanical devices of Chambers patented in 1849, and the principles of initial tension, as expounded in Rodman's publication of the same year, have been developed, at least in this country, only since the appointment of the Gun Foundry Board by Secretary Chandler, and whose manufacture was then rendered possible only through the perfection which our machine tools had attained and the improvements achieved in the metallurgy of steel. Small caliber rifles, with steel or german-silver mantled bullets, which are sighted for about two miles, and whose projectile will pierce six men, standing one behind the other in close order, at 1,000 yards. And finally to the invention of range-finders or telemeters, through which by trigonometric or mechanical methods, the position of the far distant targets now in range of new weapons may be located with precision.

For it is evident that to use these precise and powerful weapons and instruments, with the accuracy and rapidity they are capable of, the atmosphere must remain clear, and the piece must remain clean, while at the same time the highest attainable velocity must be imparted to the projectile without an undue strain being brought upon the gun. Yet we have seen that Noble and Abel found that military gunpowder gives off, on combustion, fifty-seven per cent. by weight of ultimately solid matter which is either thrown into the atmosphere to produce smoke or left as a residue to foul the bore. How considerable this smoke producing capacity of gunpowder is may be estimated if we take a Gatling firing 1200 rounds of small arm ammunition per minute (and this by no means expresses the highest attainable speed to-day) and assume that all the solid matter is driven out the gun, when we shall find that each minute six and six-tenth pounds of finely divided solid matter will be projected into the atmosphere. Add to this, in a general engagement, the smoke from the great guns, which, as with the 110-ton gun, can project 528 pounds of this solid product at each discharge, and that coming from the rapid

fire, and magazine rifles, and it is obvious that unless a favorable breeze is blowing or other favorable atmospheric conditions prevail, the force or ship will soon be enveloped in an opaque cloud of smoke and be at the mercy of an invisible foe. It is, I repeat, conditions such as these which have rendered smokeless powder, of good ballistic qualities, a great desideration, if not an absolute necessity.

While the development of the projectile, the musket, the machine gun, and ordnance; the perfection in the compositions, forms, and manufacture of gunpowder; and the invention of the instruments and devices for gauging and controlling their performance was going on, chemists were engaged in adding their contributions to the fund of human knowledge in the field of explosives. In 1788 Hausmann discovered "picric acid," in 1800 Howard discovered mercuric fulminate, in 1845 Schönbein discovered gun cotton, in 1845 Sobrero discovered nitroglycerin, in 1875 Nobel invented explosive gelatine, and in the meantime, or subsequently, numerous allied nitro-substitution compounds, nitric ethers and diazo-bodies, less generally known than those above enumerated, were produced, and identified, and shown to possess explosive properties.

The earlier experimental tests of these bodies proved that not only were some of them more powerful or more violent explosives than gunpowder, but that no smoke accompanied their explosion, since the products of their explosive decomposition were gases or vapors at the prevailing temperatures and efforts were put forth soon after their discovery to adapt them for use as propellents. These, together with various organic solids, and liquids to serve as solvents and hardening agents and ammonium and barium nitrates to serve as oxidizing agents were known and at hand.

The earliest experiment with smokeless powder was probably that made by Howard, in 1809, when he tested the properties of his newly discovered mercuric fulminate and found that though this violent agent produced little smoke, imparted a low velocity to the projectile and but a slight recoil to the piece, it burst the chamber, and demonstrated its unfitness to compete with gunpowder as a ballistic agent. Nevertheless this substance has since found a limited use, when mixed with solid diluents which act as restrainers, in ammunition for parlor rifles, and it is noticeable that when firing this ammunition there is little smoke and a scarcely audible report attending the discharge.

In 1806 Grindel carried out a somewhat extended series of experiments with a view to substituting ammonium nitrate for potassium nitrate as the oxidizing agent in gunpowder mix-

tures but the deliquescent character of the ammonium salt rendered the powder made with it useless under the then existing conditions, and has proven a formidable obstacle to its use in many of the attempts subsequently made. The fact, however, that the products of its combustion, at the prevailing temperature, are wholly gaseous rendered it a tempting material to inventors of smokeless powders and it has been more recently used, among others, by F. Gaens, who, in 1885, patented, in Germany, his so-called "Amide Powder," produced by mixing eighty parts of ammonium nitrate and 101 parts of potassium nitrate, with forty parts of charcoal. He claimed that this mixture was not hygroscopic and was practically smokeless, and he held that by the reaction consequent on the ignition, a potassamine was formed which was both volatile and explosive. Whatever the nature of the reaction, it appears from the reports that an ammonium nitrate powder was produced about this time in Germany and later in England, under the name of Chilworth Special, which possessed remarkable ballistic properties and yielded comparatively little smoke, which speedily dispersed, and which bore exposure very well until the humidity of the atmosphere approached saturation.

It is possible that the ammonium nitrate used may have been produced by Benker's process, in which the salt is formed by metathesis from solutions of sodium nitrate and ammonium sulphate exposed to a temperature of —15°, or below, for it is claimed that the ammonium nitrate which crystallizes out under these circumstances is of extraordinary purity and not at all hygroscopic.

It would appear that though these ammonium nitrate powders are slightly hygroscopic, they may retain their good qualities for long times in the hermetically sealed cases used in fixed ammunition up to the six-inch rapid fire gun, but that we know that the small amount of water necessarily present produces marked changes during long periods of storage with varying temperatures and that the ammoniacal salts attack the copper of the shells. Besides, too, we must remember that ammonium nitrate in common with other ammonium salts gives off ammonia, when heated or exposed to the air, and becomes acid so that we are debarred from using it in the presence of any bodies affected by the acid.

The next step toward the development of our modern smokeless powder was taken when, soon after the discovery of guncotton, in 1845, attempts were made to use this material as a propellent. These experiments were made in Germany, France, and England, and a very extended series were carried on by

Major Mordecai, at the Washington Arsenal, but the material, owing to its form and the imperfection in its manufacture, proved too brisant and too irregular in its action, and so unstable on keeping as to undergo decomposition in storage. The material having been proved to possess many valuable qualities was not wholly abandoned, but it continued to be the subject of study by many chemists until in 1862, it seeming that Baron von Lenck had so perfected the methods for its manufacture and purification as to ensure stability and uniformity of composition. Austria adopted it as a propellent and supplied thirty howitzer batteries with guncotton cartridges.

This is the first instance in which a really smokeless powder was employed on any but an experimental scale and this powder foreshadowed in its composition and many of its characteristics, the best modern powders of the smokeless class. The guncotton as then made retained the fibrous condition of the original cotton and in the Austrian cartridges it was spun into thread and woven into circular webs like lamp wicks, or braided, or wound on wooden or paper bobbins, and so arranged in the piece as to secure the desired air spacing as well as to insure ignition from the front. As thus used, it was claimed to be uninjured by dampness; to require a charge of but one-fourth to one-third of that of the powder previously employed; to be capable of being regulated so as to produce widely varying effects at will; to leave no residue to foul the piece; and to produce no smoke, while the gases evolved were less injurious to both the piece and men serving it than those of gunpowder. At the same time it produced less heating effect on the gun.

Unfortunately, about this time, the factory at Hirtenberg, where the guncotton was made, blew up for some undiscovered cause, and accidents having occurred with the guns, the use of guncotton was abandoned by the Austrians.

Its fate seemed now to be sealed, but such was not the case, for the scene of action then passed to England, where Abel not long after succeeded in effecting a more complete purification of the body by pulping it prior to the final washing processes, thus cutting the tubular fiber into short lengths and rendering it possible to remove the last traces of acid retained within the tubes by capillarity and which had been the occasion of its decomposition with time. Having thus obtained his pulped, purified guncotton he compressed it into such forms as was desired, and in 1867 and 1868 he obtained with it some very promising results when used with field guns. But although comparatively small charges often gave high velocities of projection without any indications of injury to the gun, the uniform fulfillment of the

conditions essential to safety proved then to be beyond control, and the military authorities not being, at that time, alive to the advantages that might accrue from the employment of a smokeless explosive in artillery, experiments were discontinued not to be resumed for nearly twenty years, and use was found for compressed guncotton in military and naval mining and especially in filling torpedoes, where it has been found the most efficient and satisfactory explosive thus far applied to this purpose.

But sportsmen, to meet whose wants and wishes many noteworthy improvements have been made in the arts, did appreciate the value, to marksmen, of smokelessness combined with high velocities and absence of fouling, and the progress made during the succeeding twenty years in the adaptation of organic nitrates to use as propellents was under their patronage and in response to their demands, and naturally, the first object sought was to so restrain the violence of the explosive that rupturing explosions, such as had occurred, could not be induced under the conditions in which the powder was to be used.

One of the first to realize a considerable degree of success was Captain Schultze, of the German artillery, who made a powder from well purified and partly nitrated wood. For this purpose he sawed the wood into sheets about one-sixteenth of an inch in thickness, which were passed through a machine that punched out discs or grains of uniform size. The grains were then deprived of their resinous matter by being boiled in sodium carbonate, washed, steamed, and then bleached with chloride of lime, when finally, after drying, the cellulose was nitrated in an acid mixture, such as is used for making guncotton. The nitrated wood was then steeped in a solution of potassium and barium nitrates, and when dry the powder was finished. By this means a nitrocellulose was produced which was diluted with unconverted cellulose and metallic nitrates, which were so intimately mingled that a fairly even rate of combustion was obtained though abnormal results were not wholly avoided.

The advantage of using nitrates and combustible organic substances as diluents was soon recognized; and, as a consequence, many powders of this nature were devised, some thirty of them having been produced and many of these put on the market, in which we find that potassium, sodium and barium nitrates, and potassium chlorate were used as oxidizing agents and sugar, cellulose, charcoal, sulphur, starch, dextrin, gums, resins, and paraffine as combustible diluents and cementing agents. All, however, approximated black gunpowder, as regards physical

structure and none attained to complete success as regards uniformity of fire and reliability of pressure.

In 1882 Messrs. Reid and Johnson patented the process for making E. C. powder, in which the pulped nitrocellulose and nitrates was agglomerated into grains by revolving the moistened mass in barrels, drying the grains, moistening with ether to harden them, and then coloring them with aurine.

About 1885 Messrs. Johnson and Borland produced the J. B. powder, in which a new idea, as regards powder manufacture, was introduced, though it had been used elsewhere for many years. The inventors mixed nitro cotton with barium nitrate and with or without charcoal or torrefied starch and granulated the mixture in a revolving drum, while the water was admitted in a fine spray. When granulated the grains were dried and then moistened with a solution of camphor in petroleum spirit, and after a time heated in a water jacketed vessel to evaporate the benzine, and the bulk of the camphor. By this treatment the grains were hardened and rendered more slowly inflamable.

As this method of treatment resembles in some particulars that followed in the production of celluloid, though it differs in details, and as several of the smokeless powders are made by methods which are adapted from this art, you will pardon me if I briefly describe it.

Celluloid is made from that form of cellulose nitrate known as nitro-cotton or soluble guncotton, and which is produced by immersing unsized and uncalendered tissue paper for a short time in a comparatively weak acid, both being kept at a moderately high temperature. This nitro-cotton is pulped in a rag engine, dried and moistened with camphor spirits. If a considerable portion of camphor spirits be added, and the mixture be allowed to stand for awhile, the mass becomes converted into a soft translucent amber gum; with more of the spirit the nitro-cotton will be completely dissolved; but as carried out, the proportion of spirit added is insufficient to produce a very apparent change.

The mixture is now taken to incorporating rolls or "grinders," (as they are called in the caoutchouc industry), where it is intimately mixed and well pressed; when the particles cohere and the whole becomes converted into a plastic, translucent homogeneous mass which behaves like India rubber and resembles it superficially in every particular but color. After incorporation, by cutting the length of the roll, the mass may be stripped off in one continuous, coherent sheet, which on exposure to the atmosphere, through which the spirit and camphor are volatilized, hardens to a hornlike mass.

In the manufacture of a smokeless powder by this means, it is customary to mix with the nitro-cotton or mixed cellulose nitrates, a small proportion of other nitrates in order to effect complete combustion and a restrainer to assist in bringing the rate of combustion within normal limits; and this mixing is easily effected on the incorporating rolls. Barium nitrate is the salt which is perhaps most largely used, and it is preferred because it is very permanent, contains a fair proportion of available oxygen which it yields with comparative readiness, and possibly because the carbonate which is formed by the combustion has so high a specific gravity that it settles with considerable speed.

Other solvents besides camphor spirits are employed when the higher cellulose nitrates are used in the manufacture of the powder. Thus Engel takes a cellulose nitrate prepared from wood, while Glaser employs that prepared from paper or cardboard and treats it, when dry, with ethyl acetate or acetone, the action of the solvent being aided by mechanical kneading in a suitable vessel until a viscid paste or gelatinous mass is obtained with which the barium nitrate and a hydrocarbon, such as naphthalene, is incorporated. The mass is then formed into any desired shape and the solvent is allowed to evaporate or is distilled off by any suitable means when the powder is left as a dense horny material, with a glassy fracture, which can be readily granulated.

The first military smokeless powder of the modern class was made in France in 1886 by Vieille, and is said to have been compounded of cellulose nitrates mixed with picric acid, but it was soon abandoned in favor of the Poudre B., which consisted of cellulose nitrates alone, or Poudre B. N., which consisted of these nitrates mixed with barium nitrate and potassium nitrate as oxidants, and sodium carbonate as a neutralizer. Both these mixtures were condensed and hardened to a celluloid-like mass by means of a solvent like ether-alcohol, ethyl acetate or acetone.

Excellent ballistic results have been reported from France as being obtained with these powders, and they have been adopted by the French government. At the same time similar mixed cellulose nitrate powders have been produced and used in Germany, Austro-Hungary and Switzerland; the Weteren, Troisdorf and Von Förster powders being of this class. Notwithstanding that these have so long been known, our government has, with regal graciousness, recently granted a patent to two of its officers for a powder of this composition.

These are made by mixing the ingredients together with the

solvent in a kneading machine of the Werner and Pfleiderer class, in batches of one to two hundred weight, until it is converted into a dough, when it is incorporated and the solvent partly driven off by putting on the grinding rolls, by which means it is also formed into continuous sheets, whose thickness is fixed by the set of the rolls. It is preferable where thick masses are desired to first roll into thin sheets so as to evaporate the solvent as completely as possible from the gelatinized mass, and then by piling the thin sheets on one another, weld them together by running them through the rolls. They are then granulated by passing them under a set of revolving circular knives which cut them first into strips and then into rectangles of the desired size and shape. These powders are dense, hard and hornlike in appearance.

Following Vieille by about two years,[1] Nobel invented ballistite, which practically is a modified explosive gelatine, differing from it only in that while the gelatine consists of ninety-three per cent. of nitroglycerin, and seven per cent. of nitro-cotton, ballastite contains about forty per cent. of nitro-cotton and one to two per cent. of anilin or diphenylamin, which is added to the nitroglycerol nitro-cotton mixture as a neutralizing agent to ensure stability. At first the solution of the gun-cotton and gelatinization of the mixture was effected by means of camphor and later by means of benzene, but it is now produced under the English patent of Lundholm and Sayer of 1889. They discovered that while dry nitro-cotton is but slightly soluble in nitroglycerin even at moderately high temperatures, when mixed with warm water and stirred up by compressed air, gelatinization sets in and solution may be completed by pressing out the water and working in the grinder. Flexible, transparent rubber-like sheets are formed, which may be cut into flakes in cutting machines of the usual type, or in pastry cutters, or may be squirted through spaghetti machines, as is done in Italy, where these cords or threads of ballistite are known as "Filite."

It is curious to note how many of the machines devised for bread making, pastry cutting and macaroni forming, have been employed in the manufacture of smokeless powder.

In 1889 Sir Frederick Abel and Professor James Dewar secured their patents on cordite, which like ballistite, contains nitroglycerin and cellulose nitrate, but whereas ballistite is made from nitro-cotton alone, cordite is made from "gun-cotton" containing from ten to twelve per cent. of nitro-cotton, to which is added a little tannin, dextrin or vaseline to serve as a restrainer. The gelatinization is effected by means of acetone,

[1] English Patent, January 31, 1888.

the mixture being kneaded to a dough in a water-jacketed kneading machine, compacted in a mould in a preliminary press, and the mould transferred to a spaghetti machine, where the explosive is squirted into cords. As these cords issue, they are reeled on bobbins, which are placed in the drying house to drive off the acetone. When this is completed the product of ten pressings is wound from ten one-strand reels on to one ten-strand reel and then the cordite on six ten-strand reels is wound on one drum, making a cord of sixty strands, which in short lengths forms the thirty and one-half grains charge for the magazine rifle. For the higher calibers the cords are cut in lengths as they issue from the press, dried and made up into bundles. Cordite is an elastic rubber-like mass with a light to dark brown color.

Analogous to these in composition, in that they consist of nitroglycerin with cellulose nitrates, are many powders, such as amberite, Maxim's powder, Leonard's powder, P. P. G., Peyton's powder, German smokeless powder and others, and they differ in but slight particulars. Thus Curtis and André *blend different cellulose nitrates* before incorporation so as to secure a definite nitrogen content, and then cement by ether-alcohol; Maxim restrains his powder with castor oil; Leonard restrains his with lycopodium, and adds urea crystals as a neutralizer; Walke claims to make P. P. G. from a nitro-cellulose, which is not gun-cotton, and so on.

The employment of nitro substitution compounds as bases for smokeless powders has been comparatively limited. Over twenty years ago Designolle invented powders made by mixing potassium picrate, potassium nitrate and charcoal in various proportions. Borlinetto produced them from picric acid, sodium nitrate and potassium dichromate. Abel and Brugère from ammonium picrate, potassium nitrate and charcoal, and more recently Nobel from ammonium picrate, barium nitrate and charcoal. Within a few years past a powder has been manufactured in this country and put upon the market as a sporting powder, which was composed of ammonium picrate, potassium picrate, and ammonium dichromate, but I understand it has given such irregular and abnormal pressures that its manufacture has been discontinued.

While these powders may have been smoke-weak as compared with gunpowder, it is difficult to understand how, in the presence of such amounts of metallic radicles, they could have been smokeless. A powder, however, which is made by Hermann Güttler, by dissolving nitro-lignin in molten dinitro-toluene and which he calls Plastomentite, may well possess this property,

and it is reported to have given good ballistic results at the Bucharest tests of 1893.

The powder called Gelbite, and invented by Dr. Stephen H. Emmens, was also smokeless. This was made by an ingenious process in which paper in strips was nitrated to a moderate degree of nitration, then fumed with ammonia to neutralize the acid, and then treated with picric acid to neutralize the ammonia and form ammonium picrate. These strips were then rolled up into rolls as charges, but as might have been foreseen from a study of the behavior of gunpowder in guns and the study of the history of gun-cotton, this powder was too brusque in action and has been abandoned.

I began my own experiments with smokeless powder manufacture in 1889. At this time the remarkable results published from France, and the announcement that that country had adopted a smokeless powder, had produced their desired strategic effect. All her rivals were seeking to be equally well equipped and were hastening to adopt a powder even before its qualities were thoroughly proven. The newspapers contained remarkable accounts of their performances and alleged descriptions of their methods of production, which while interesting as news and conveying valuable suggestions, could not be relied upon as to accuracy in details.

At the outset, being familiar with the impossibility of securing absolute uniformity and constancy of composition in physical mixtures like gunpowder, and realizing how important this feature was with our precise modern weapons, and when employing an explosive possessing great energy, I determined to attempt to produce a powder which should consist of a single substance in a state of chemical purity. This was a thing which I had not known of having been done, nor have I yet learned that any one else has attempted it. Among the bodies at command, the nitric ethers seemed most available, and of these cellulose nitrate seemed for many reasons the most promising.

There are, as you are aware, several of these nitrates (authorities differ as to the number) which differ in their action towards solvents, though all except the most highly nitrated are soluble in methyl alcohol. In the commercial production of cellulose nitrate certainly, and so far as I have observed under all circumstances, when nitrating cellulose the product is a mixture of different cellulose nitrates. Even in the perfected Abel process for making military gun-cotton, as carried out at the Royal Gun Powder Factory, at Waltham Abbey, according to Guttmann[1], the product contains as a rule, from ten to twelve per cent. of nitro-cotton.

[1] Manufacture of Explosives, 2, 259, 1895.

Consequently I began by purifying my dried pulped military gun-cotton, which was done by extracting it with hot methyl alcohol in a continuous extractor, and when this was completed the insoluble cellulose nitrate was again exposed in the drying room. The highly nitrated cellulose was then mixed with a quantity of mono-nitro-benzene, which scarcely affected its appearance and did not alter its powdered form. The powder was then incorporated upon a grinder by which it was colloidized and converted into a dark translucent mass resembling India rubber. The sheet was now stripped off and cut up into flat grains or strips, or it was pressed through a spaghetti machine and formed into cords, either solid or perforated, of the desired dimensions, which were cut into grains. Then the granulated explosive was immersed in water, boiling under the atmospheric pressure, by which the nitro-benzene was carried off and the cellulose nitrate was indurated so that the mass became light yellow to gray, and as dense and hard as ivory, and it was by this physical change in state, which could be varied within limits by the press that I modified the material from a brisant rupturing explosive to a slow burning propellent.

This is the powder which I styled indurite, and which has been popularly known as the Naval Smokeless Powder.

I was satisfied that I was justified in starting on this new practice in powder-making when I found, on examination of the samples of foreign military powders[1] which later began to reach me officially, that they were heterogeneous mixtures as the old gunpowder is and that they contained matter which was volatile at ordinary temperatures, and when I learned that the nitroglycerin powders cracked from freezing.

I was still more satisfied when I learned the results of the proving tests which were all made except the chemical stability and breaking down tests by naval officers detailed for this purpose at the Proving Ground and elsewhere, and who had no prejudice in its favor. All of the numerous publications which have appeared about it have issued from headquarters, and I present the matter myself here for the first time.

I have appended the data from these trials to this address where, on inspection it will be seen, that after development, the powder in use, in successive rounds, gave remarkably regular pressures and uniform velocities. I was informed by the Chief of the Bureau before the firing trials, recorded in the tables began, that if I could produce a powder giving 2,000 feet initial velocity and but fifteen tons pressure, it would be a complete success. Inspection of the tables show that this was more than realized and that in two successive rounds in the

[1] Table I.

six-inch rapid fire gun, using twenty-six pounds of my powder and a 100 pound projectile, the pressures were 13.96 and 13.93 tons, and the velocities 2,469 and 2,456 feet per second respectively, while according to the Report of the Secretary of the Navy, 1892, page 26, "the powder manufactured for use in the six-inch rapid fire guns was stored at Indian Head proving ground, through a period of six months, covering a hot summer, and at the end of the time showed no change in a firing test."

On page 25 Secretary Tracy says, "It became apparent to the department early in this administration that unless it was content to fall behind the standard of military and naval progress abroad in respect to powder, it must take some steps to develop and to provide for the manufacture in this country of the new smokeless powder, from which extraordinary results had been obtained in Europe. With this object negotiations were at first attempted looking to the acquisition of the secret of its composition and manufacture. Finding itself unable to accomplish this, the Department turned its attention to the development of a similar product from independent investigation. The history of these investigations and of the successful work performed in this direction at the torpedo station has been recited in previous reports. It is a gratifying fact to be able to show that what we could not obtain through the assistance of others, we succeeded in accomplishing ourselves, and that the results are considerably in advance of those hitherto attained in foreign countries."

From this survey we see that all of the smokeless powders that have met with acceptance and proved of value as ballistic agents with the exception of Indurite are mixtures of one or more of the cellulose nitrates, or mixtures of these bodies, with nitroglycerin or some other oxidizing agent, like barium nitrate, and a restrainer or with a nitro substitution compound and that all have been condensed or hardened into a rubber-like or celluloid-like form, by which, even under the high pressures which obtain in the gun, they are expected to undergo combustion only and that at a moderate and regular rate.

In thus condensing the material, and in determining the best form of grain, it will be observed that we have been guided by the experience gained in the compression of gunpowder, and we have been able to effect this as we have by the experience gained in the development of celluloid, and we have been able to manipulate our product and shape it into grains only by adopting the methods and machines developed in the manufacture of food, while we have been able to test our product and check our results and thus ensure a more rapid and

certain advance by the constant use of the pressure gauge and velocimeter. In my opinion, if these resources had not been at command and available the smokeless powder industry would not yet exist.

From what has been said it may properly be inferred that we seek in these new powders all the virtues of the old gunpowder with the addition that the new powder shall be smokeless, impart higher velocities while producing no greater pressures and that less of it shall be required to do the work. These requirements may be summed up as follows:

The conditions that a smokeless powder suitable for a propellent should fulfill are:

1. That it shall be physically and chemically uniform in composition.

2. That it shall be stable and permanent under the varying conditions of temperature and humidity incident to service storage and use for all time.

3. That it shall be sufficiently rigid to resist deformation in transportation and handling.

4. That it shall produce a higher or as high a velocity with as low a pressure as the service charge of black powder for a given piece.

5. That it shall be incapable of undergoing a detonating explosion.

6. That the products of its combustion shall be nearly if not quite gaseous so that there shall be no residue from it and little or no smoke.

7. That it shall produce no noxious or irrespirable gases or vapors.

8. That it shall not unduly erode the piece by developing an excessive temperature.

9. That it shall be as safe as gunpowder in handling and loading.

10. That it shall be no more than ordinarily dangerous to manufacture.

Most of these requirements have been satisfied in several of the powders, but time alone can determine the question of absolute stability and especially as the comparison is instituted with gunpowder which has been under observation for over 500 years.

We can and do apply tests whose results give us some confidence as I did when I exposed Indurite wrapped in felt in an iron vessel to a temperature of 208° F. for six hours without its undergoing change, and again at a temperature of 212° F. for twenty hours before any change was observed, and again to 5° F. without its being affected.

In fact from the outset I have advised the application of most rigid tests and drew up the following scheme for the Navy Department in July, 1891, by which to test Indurite.

"The most important requisite of powder, after passing the proof test, is that it shall retain its characteristics under all the conditions of storage or transportation which may obtain in the service or that, if any change does take place, it shall not cause the powder to develop under the "proof" conditions any greater pressure than it did at the time of proving, and that such falling off in velocity as may result from this change in the powder shall not be relatively greater than that which obtains for service black powder, and shall be uniform for the same conditions of exposure.

"In providing for this test I would first prove a ten pound lot to determine the maximum weight that will come within the limits fixed for pressure and velocity, and then I would load 1000 Winchester 30.1 cal. and 1000 Mannlicher shell with a charge some grains (say five) less than the maximum, so as to be doubly safe in case the pressure should become increased through the treatment to which the powder is subjected.

"The loading should be done with extreme care by skilled workmen in an especially clean and uniformly heated and dried room. The charges should be weighed on chemical balances and with all the precautions surrounding an analytical operation. The balls should be weighed and gauged, and the shell should be gauged so as to secure as nearly absolute uniformity as possible, while the caps and priming (if used) and wads should be identical for each shell of each 1000 lot.

"These being prepared, I would pack these ball cartridges precisely as if ready for issue to the service, and then I would store 385 Winchester's and 385 Mannlicher's in the regular magazine at the Naval Torpedo Station, and the same number of the same kind in the regular magazine at the Naval Ordnance Proving Ground. I would then draw from the magazine at the Torpedo Station twenty-five Winchester's and 25 Mannlicher's and fire them, using the muskets and measuring instruments which are to be used throughout the trials, and I would repeat this trial every month for three years, firing ten rounds of each form of ammunition and using the same muskets and instruments throughout. At the same time I would have an identical set of tests made at the Proving Ground, the same precautions being taken there regarding the instruments and tools. Throughout the tests a close watch should be kept on the magazines by means of maximum and minimum thermometers so that if abnormal results are obtained in firing it may be known whether or

not any abnormal conditions have obtained in the magazine. This series of tests will consume 1540 rounds. It would, in my judgment, be of much value to store with these cartridges and fire with them an equal number of charges of standard service black powder, to be used as a standard for reference by which any error in the observations, or defects in the instruments may be detected.

"I would take eighty rounds of the Winchester's and eighty of the Mannlicher's and place them in an oven heated to 140° F. or thereabouts. At the end of one month twenty of each are to be drawn out and this to be repeated each month for four months. One half of each form should be proved at the Torpedo Station and the other half at the Proving Ground.

"I would take eighty rounds of the Winchester's and eighty of the Mannlicher's and subject them for two weeks to the freezing temperature, then for two weeks to a temperature of about 140° F., and then draw twenty of each, and this should be continued until the last forty drawn out have been exposed for eight weeks to freezing and eight weeks to the high temperature. The firing trials with these should be made as with preceding ones.

"The remaining shell should be stored in the regular magazine to be used in any test case which may arise or in any manner suggested by the results obtained in the tests described above.

"In the meantime tests could be made with the hand cut S. P. for the capacity of the powder to resist crumbling and dusting during transportation and the tendency of the fixed ammunition to explode *en masse* by the impact of projectiles, or by the explosion of a single cartridge in the midst of a box filled with them. The first can be effected by taking a pound or a kilogram of carefully sifted powder, placing in a copper vessel which it only partly fills, and attaching it to a shaft so that it will be continually and violently shaken, and allowing this to go on every working day for a week. The powder can then be sifted, using the same mesh as before, the weight of the dust found and the percentage of dusting for the given circumstances determined.

"In the trials for tendency to explode *en masse* fifty or forty-five caliber ammunition can be used and the weights of charges need not be very precise, but the ammunition should be packed in, as nearly as possible, the same way as would obtain in service practice."

We have seen that the development of smokeless powder has been rendered necessary by the improvement in the gun. It now appears that in consequence of the possession of the powder

we must further improve the gun for we cannot in our present guns utilize all the energy now available. Experiments looking to this have been going on in France, where in a Canet ten cm. gun of eighty calibers, with a charge of 12.35 pounds of powder and a projectile weighing 28.66 pounds there was obtained the extraordinary muzzle velocity of 3366 feet per second, while the maximum pressure was 18.91 tons per square inch. Longridge, an English authority, deprecates the lengthening of the gun as it becomes too unwieldy and he advocates utilizing the energy of the gun by strengthening it so it will endure greater pressures and then using larger charges. He points out that if this Canet gun were reduced to forty-five calibers, and strengthened, we could obtain from it the same enormous muzzle velocity by increasing the charge to thirteen and a half pounds, though the pressure would rise to twenty-five tons per square inch.

What the result will be where authorities of standing disagree is impossible to foresee, but the fact is demonstrated that the powder is now more highly developed than the gun, and that while seeking for smokelessness, we have secured a propellent which is capable of producing much higher velocities than gunpowder, with all the additional advantages of flat trajectory, increased danger area, greater accuracy, and greater range which follow as consequences.

TABLE I.

COMPOSITION OF VARIOUS POWDERS.

Mark.	Nitro-Cotton.	Guncotton.	Barium Nitrate.	Potassium Nitrate.	Sodium Carbonate.	Volatile.	Cellulose.	Sodium Picrate.	Charcoal.	Humus.	Nitro-Glycerin.	Graphite.
B. N., Aug. 22, '90	26.84	44.42	18.25	3.08	4.92	2.05	....	....	....	....	....	....
B. N., Dec. 5, '90	29.79	40.54	19.00	5.81	3.87	1.50	....	....	....	....	....	....
B. N., June 3, '91	38.05	35.55	18.94	1.81	4.51	1.06	....	....	....	....	....	....
B. N., Aug. 12, '91	41.31	29.13	19.00	7.97	2.03	1.43	....	...	....	....	....	....
B. N., Oct. 16, '91	31.38	49.89	17.92	3.43	2.82	0.82	....	....	....	....	....	....
B. N_A., July 9, '90	31.27	40.52	18.42	6.62	2.58	1.25	....	....	....	....	....	....
B. N_C., Aug. 22, '90	32.62	39.44	18.90	7.45	1.39	1.63	....	....	....	....	....	....
B. N_C., Dec. 5, '90	32.03	39.52	19.36	5.17	3.75	0.92	....	....	....	....	....	....
B. N_I., Oct. 16, '91	72.09	26.49	....	....	....	0.92	0.47	trace	....	....	....	....
French Powder, June 3, '91	73.11	25.98	....	. .	....	0.89	....	trace	....	....	....	....
Poudre B., Oct. 16, '91	32.86	66.00	....	....	....	1.14	trace	....	....	....	....	....
Walsrode, S. P., Sept. 4, '90	12.08	86.28	....	....	0.93	0.72	....	....	....	....	....	....
[1]Wetterin, S. P., March 18, '91	46.70	30.35	....	....	....	9.66	....	....	12.39	0.90	....	....
[2]Wetterin, S. P., March 18, '91	48.15	30.73	....	....	....	8.22	....	....	12.12	0.77	....	....
[3]Wetterin, S. P., March 18, '91	47.78	25.87	....	....	....	14.69	...	....	10.84	0.80	....	....
Lebel, Sept. 27, '90	28.21	69.45	....	....	0.80	1.49	....	....	....	....	....	....
German, Oct. 15, '90	10.00	88.43	....	....	0.56	0.99	trace	....	....	....	....	....
Cordite, Sept. 17, '90	7.04	29.20	....	....	[4]6.17	1.30	0.23	....	....	....	56.04	....
Cordite, Oct. 11, '90	8.45	27.72	....	....	[4]4.23	1.45		....	....	....	58.13	....
Ballistite, Sept. 19, '90	44.58	....	....	....	2.44	....	....	....	....	....	52.99	....
Nobel's, S. P., Oct. 15, '90	53.26	0.97	....	....	3.42	0.41	....	....	....	....	41.95	....
Schwab, Nov. 7, '90	77.41	20.42	....	....	0.69	1.47	....	....	...	...	....	trace

[1] Small arm. [2] Small cube. [3] Large cube. [4] Includes dextrine.

Mark.	Nitro-Cotton.	Guncotton.	Barium Nitrate.	Potassium Nitrate.	Sodium Carbonate.	Volatile.	Cellulose.	Sodium Picrate.	Charcoal.	Humus.	Nitro-Glycerin.	Graphite.
[1] Reg. Y., 283, Nov. 14, 90	56.46	....	....	....	0.37	0.33	....	....	....	....	42.84	trace
[2] Reg. Y., 283, Nov. 14, '90	52.10	....	....	...	0.36	0.39	....	....	....	....	47.17	....
German, S. P., Aug. 7, '91	48.83	7.45	....	....	....	0.53	....	....	....	....	43.15	trace
Maxim, flat, June 3, '92	8.14	71.19	....	....	2.58	0.19	....	....	....	....	[3]17.90	....
Maxim, cord, June 3, '92	6.84	46.60	....	....	1.70	0.26	....	....	....	....	[3]44.60	....
									Manchester yellow			
Rifleite, May 7, '92	22.48	74.16	....	....	....	0.84	....	....	2.52	....	....	trace
									Aurine			
S. K., May 6, '92	20.39	57.73	18.08	1.24	....	1.43	....	....	1.11	....	....	....
S. R., May 7, '92	28.18	46.97	19.97	2.35	....	1.45	....	....	1.c6	....	....	....
	[4]lignin	[5]lignin			$NaNO_3$		[6]lignin		Aurine			
E. C., Nov. 9, '91	53.57	1.86	34.26	1.48	3.07	1.17	3.12	....	0.55	....	....	....
									Paraffin			
Schultze, Sept. 24, '91	27.71	32.66	27.62	2.47	2.88	1.48	1.63	....	4.20	....	....	....
Brackett, Sept. 26, '91	31.43	13.70	....	....	19.76	2.93	13.22	....	....	18.94	....	....
American Wood Pd., Jan. 27, '91	24.90	30.07	....	....	9.76	5.83	19.55	....	....	9.89	....	....
" Grade C., Aug. 27, '91	29.25	14.06	....	....	15.27	3.01	28.08	....	....	10.32	....	....
" " E., Aug. 27, '91	24.91	25.62	....	....	17.81	3.86	19.15	....	....	8.65	....	....
" 10-Bore Trap, Aug. 29, '91	33.21	18.69	....	....	14.82	2.36	20.27	....	....	10.65	....	....
" 12-Bore Trap, Aug. 31, '91	29.47	21.85	....	....	13.38	3.14	16.59	....	....	15.62	....	....
					sodium picrate				Charcoal			
Reine Powder, Dec. 8, '90	....	....	48.44	....	46.31	1.18	....	....	4.07	....	....	....

[1] Five mm. [2] One mm. [3] Includes castor oil. [4] Soluble nitro-lignin. [5] Insoluble nitro-lignin. [6] Unconverted lignin.

TABLE II.

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	Gun.	Weight of Charge.		Projectile. System.	Projectile. Weight.	Pressure. Tons.	Velocity. Foot—seconds.
Service Black.	Hotchkiss 1 Pdr.	140 grams		Housing	465 grams	11.2	1694
"	"	150 "	Small ignition disk in each charge.	"	450 "	11.2	1690
"	"	150 "		Common shell	450 "	....	1793
"	"	150 "		"	450 "	....	1841
S. P. No. 151, No. 3 T.	"	50 "		"	450 "	....	1341
"	"	70 "		"	450 "	....	1811
"	"	80 "		"	450 "	....	2150
"	"	80 "		Housing	460 "	13.0	1877
"	"	80 "		"	460 "	15.0	1896
"	"	75 "		Common shell	450 "	....	1816
"	"	75 "		"	450 "	....	1760
"	"	75 "		"	450 "	....	1894
S. P. No. 153, No. 4 T.	"	70 "		Housing	465 "	14.2	1774
"	"	70 "		"	465 "	14.4	1616
"	"	70 "		Common shell	450 "	About 12.13 tons	1774
"	"	70 "		"	450 "	"	1776
S. P. No. 157, No. $4\frac{3}{16}$ T.	"	70 "		Housing	465 "	8.2	1082
"	"	90 "		"	465 "	11.2	1363
M. N. 2.	"	100 "	Ignition charge 8 grams. N. X. 9 (Blk. fine grain). Ignited at rear.	"	....	13.5	Lost—missed wires
"	"	90 "		Common shell	Not obs.	Not obs.	1584
"	"	90 "		"	....	9.0	1281
S. P. No. 140.	Hotchkiss 3 Pdr.	100 "		"	3 pounds	1.5	882
"	"	200 "		"	3 "	4.3	Lost
"	"	300 "		"	3 "	15.0	2186
"	"	300 "		"	3 "	12.2	Lost
"	"	300 "		"	3 "	12.0	Lost
"	"	300 "		"	3 "	12.3	2105
"	"	310 "		"	3 "	14.9	2216
"	"	310 "		"	3 "	14.8	2250
S. P. No. 148.	"	275 "		"	....	....	....
"	"	300 "		"	....	9.0	1766

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	Gun.	Weight of Charge.		Projectile. System.	Projectile. Weight.	Pressure. Tons.	Velocity. Foot—seconds.
S. P. No. 148.	Hotchkiss 3 Pdr.	315 "	" " Small ignition disc. Priming 89. N. X. Q.	Common shell	....	10.4	1921
"	"	325 "		"	....	11.2	2017
"	"	335 "		"	....	12.2	2076
"	"	338 "		"	....	11.0	1995
"	"	345 "		"	....	15.4	2187
"	"	340 "		"	....	14.3	2166
"	"	340 "		"	....	11.5	2126
"	"	343 "		"	....	18.0	2214
S. P. No. 153, No. 4 T.	"	250 "		"	3.3 lbs.	11.3	1887
"	"	275 "		"	3.3 "	13.6	2051
"	"	300 "		"	3.3 "	24.0	2281
"	"	275 "		"	3.3 "	16.8	1975
"	"	270 "		"	3.3 "	14.5	2000
"	"	270 "		"	3.3 "	16.0	2018
"	"	270 "		"	3.3 "	22.5	2050
S. P. No. 141 a.	Hotchkiss 6 Pdr.	200 "	Ignition charge 8 grams N. X. L. Blk. fine grain.	"	6 "	7.2	1085
"	"	250 "		"	6 "	9.0	1237
"	"	300 "		"	6 "	9.2	1453
"	"	300 "		"	6 "	9.2	1453
"	"	325 "		"	6 "	9.6	1584
"	"	350 "		"	6 "	9.6	1648
"	"	375 "		"	6 "	13.6	1813
"	"	375 "		"	6 "	10.6	1738
"	"	400 "		"	6 "	16.0	1903
"	"	390 "		"	6 "	14.3	1841
"	"	392 "		"	6 "	14.3	1855
S. P. No. 153, No. 4 T.	"	200 "		"	6 "	6.5	1330
"	"	250 "		"	6 "	8.6	1544
"	"	300 "		"	6 "	9.9	1679
"	"	350 "		"	6 "	16.7	1728
"	"	340 "		"	6 "	15.0	Lost

Tests of Indurite at Naval Ordnance Proving Ground.

Powder.	*Gun.*	*Weight of Charge.*			*Projectile. System.*	*Projectile. Weight.*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
S. P. No. 153, No. 4 T.	Hotchkiss 6 Pdr.	340	"		Common shell	6 lbs.	18.0	Lost
S. P. No. 157, No. 4$\frac{3}{16}$ T.	"	300	"		"	6 "	5.0	1324
"	"	350	"		"	6 "	6.5	1473
"	"	400	"		"	6 "	11.4	1775
"	"	420	"	Priming 8 grams N. X. L.	"	6 "	9.1	1738
S. P. No. 148, No. 4.	"	300	"		"	6 "	7.6	1543
"	"	350	"		"	6 "	11.1	1751
"	"	365	"		"	6 "	12.0	1818
"	"	372	"		"	6 "	12.5	1835
"	"	382	"		"	6 "	11.0	1862
"	"	392	"		"	6 "	13.0	1920
"	"	410	"		"	6 "	13.6	2002
"	"	418	"		"	6 "	15.0	2047
"	"	418	"		"	6 "	15.0	2047
S. P. No. 148, No. 4.	"	418	"		"	6 "	14.8	2043
"	"	418	"		"	6 "	14.0	2012
"	"	418	"		"	6 "	13.0	1992
M. N. 2.	"	400	"		"	6 "	9.5	1724
"	"	480	"	Priming charge 25 grams of fine grained powder in each charge.	"	6 "	11.6	1988
"	"	480	"		"	6 "	12.0	1992
"	"	440	"		"	6 "	8.0	1702
"	"	450	"		"	6 "	8.0	1728
"	"	450	"		"	6 "	8.1	1735
S. P. No. 146 b.	4-in. No. 11.	4.5 pounds			"	33 "	13.5	1762
S. P. No. 146 a T.	"	4.5	"		"	33 "	10.9	1820
S. P. No. 149 T.	"	2.25	"		"	33 "	3.5	1177
"	"	4.50	"		"	33 "	10.3	1845
"	"	4.75	"		"	33 "	11.5	1945
"	"	5.00	"		"	33 "	13.6	2046
"	"	5.15	"		"	33 "	14.0	2080
"	"	5.25	"		"	33 "	14.2	2083

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	Gun.	Weight of Charge.		Projectile. System.	Projectile. Weight.	Pressure. Tons.	Velocity. Foot—seconds.
S. P. No. 149.	4-in. No. 11.	5.00 "		Common shell	33 lbs.	13.6	Lost
"	"	5.35 "		"	33 "	15.2	Lost
"	"	5.30 "		"	33 "	15.0	1943
"	"	5.30 "		"	33 "	15.0	2122
S. P. No. 159 M.	"	3.5 "	Ignited at rear.	"	33 "	9.5	Lost
"	"	4.05 "		"	33 "	10.3	1912
"	"	4.2 "		"	33 "	11.0	1936
"	"	4.8 "		"	33 "	12.0	1990
"	"	5.2 "		"	33 "	14.7	2125
"	"	5.2 "		"	33 "	14.8	2134
"	"	5.3 "		"	33 "	14.8	2145
S. P. No. 149 M.	"	5.3 "		"	33 "	15.0	2160
"	"	5.3 "		"	33 "	14.8	2158
S. P. M. N. 2 (163).	"	4 "	One ignition grain in base of each charge. Ignition at rear.	"	33 "	7.5	1591
"	"	5 "		"	33 "	10.2	1888
"	"	5.5 "		"	33 "	12.35	1993
"	"	5.5 "		"	33 "	12.35	1997
"	"	4 "		"	33 "	7.3	1606
"	"	4 "		"	33 "	7.2	1569
"	"	5 "		"	33 "	10.5	1892
"	"	5 "		"	33 "	10.2	1865
S. P. No. 159 M. N. 2.	6-in. No. 120.	9.5 "		"	77 "	6.5	1728
"	"	13½ "		"	77 "	10.0	2131
"	"	15 "		"	77 "	11.9	2281
"	"	16½ "		"	77 "	13.6	2415
S. P. M. N. 3, No. 162.	"	11½ "		"	100 "	5.0	1466
"	"	15 "		"	100 "	7.9	1784
"	"	18 "		"	100 "	11.0	2060
"	"	20 "		"	100 "	13.2	2212
"	"	21 "		"	100 "	14.4	2312
" After 6 mos. storage.	"	14 "		"	100 "	6.7	1678
"	"	20 "		"	100 "	12.0	2170

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	*Gun.*	*Weight of Charge.*		*Projectile.* *System.*	*Projectile.* *Weight.*		*Pressure. Tons.*	*Velocity. Foot—seconds.*
S. P. M. N. 6.	6-in. No. 120.	15	"	Common shell	100	lbs.	5.06	1535
"	"	19	"	"	100	"	7.30	1793
"	"	23	"	"	100	"	11.20	2151
"	"	25	"	"	100	"	12.56	2369
"	"	26	"	"	100	"	13.96	2469
"	"	26	"	"	100	"	13.93	2456
S. P. M. N. 3, No. 162.	"	7	"	"	50	"	4	1496
"	"	11	"	"	50	"	10	2108
"	5-in. "	7	"	"	50	"	4	1496
"		11	"	"	50	"	10	2108
"		12	"	"	50	"	12	2256
"		12.75	"	"	50	"	13.2	2383
"		13.12	"	"	50	"	14.2	2474
"		13.4	"	"	50	"	15.6	2578
S. P. M. N. 2 (168).	4-in. R. F. No. 8.	5½	"	"	33	"	12.4	1997
"	"	5¾	"	"	33	"	13.4	2042

ACIDITY OF MILK INCREASED BY BORACIC ACID.

BY E. H. FARRINGTON.

Received July 22, 1896.

WHILE making some investigations with milk preservatives, the writer noticed that sweet milk in which a small quantity of boracic acid (preservaline) was dissolved, required what appeared to be an abnormally large quantity of one-tenth normal alkali to neutralize it and much more than water in which the same amount of "preservaline" was dissolved. One-half gram of preservaline was dissolved in 500 cc. water, and twenty cc. of this solution required one cc. of one-tenth normal alkali to produce the pink color, when phenolphthalein was used as an indicator in titrating. Before adding preservaline the water had a neutral reaction.

One-half gram preservaline was dissolved in 500 cc. of sweet milk, and twenty cc. of it required eight cc. of one-tenth normal alkali to give the pink color, although before adding the preservaline twenty cc. of this same milk gave the pink color with only four cc. of one-tenth normal alkali.

The same amount of preservaline increased the acidity of a given quantity of milk four times as much as it did the acidity of the water.

The writer is unable to explain this reaction, but it gives a simple means of detecting preservaline or boracic acid in milk, as normal milk will smell or taste sour when it contains as much natural acidity as is represented by eight cc. of one-tenth normal alkali to twenty cc. milk. This represents 0.36 per cent. lactic acid, and it can be safely stated that milk which contains over three-tenths per cent. lactic acid and neither tastes or smells sour, has been adulterated with some preservative, probably boracic acid.

DAIRY SCHOOL,
UNIVERSITY OF WISCONSIN.

CORRESPONDENCE.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., JULY 23, 1896.

Editor Journal of the American Chemical Society, Easton, Pa.:

DEAR SIR:—A majority of the Executive Committee has decided to call the annual meeting of the Association of Official Agricultural Chemists for Nov. 6, 7 and 9, 1896. These dates immediately precede the meetings of the Association of Agricultural Colleges and Experiment Stations, which will convene in Washington, Nov. 10. The session will be held, as heretofore, in the lecture hall of the National Museum, at Washington, D. C.

The Ebbitt House offers to the Association entertainment at the rate of $3.00 per day and the free use of its parlors for committee meetings, if desired. The Ebbitt House is on the corner of "F" and 14th Sts., and can be reached from all stations by the "F" St. or Avenue cars.

Respectfully,
H. W. WILEY,
Secretary A. O. A. C.

BOOKS RECEIVED.

Bulletin No. 42. Second Series. Horticulture. Louisiana State Experiment Station, Baton Rouge, La. 1896. 44 pp.

Bulletin No. 123. Examination of Food Products sold in Connecticut. Connecticut Agricultural Experiment Station, New Haven, Conn. July, 1896. 79 pp.

Transactions of the American Institute of Mining Engineers. Vol. xxv. February to October, 1895, inclusive. New York City: Published by the Institute. 1896. xvii, 1068 pp.

Part III. Geology and Agriculture. A preliminary report upon the Florida parishes of East Louisiana and the Bluff. Prairie and Hill Lands of Southwest Louisiana. By W. W. Clendenin, A.M., M.S., Geologist. Louisiana Experiment Station, Baton Rouge, La. 96 pp.

ERRATA.

On page 667, August number, 12th line from bottom, in equation, for *o.3b* read *o.3y*.

On page 668, 2nd line from top, for *Dividing* read *Multiplying*.

VOL. XVIII. [OCTOBER, 1896.] NO. 10.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.

BY W. W. ANDREWS.

Received August 7, 1896.

IN the years 1883 and 1884 two papers were published by Dr. Eugene Haanel, of Victoria College, Cobourg, Ontario, now of Syracuse University, in the Proceedings of the Royal Society of Canada, in which he described the brilliant results he was able to obtain in the production of the Bunsen iodide films on the blowpipe support then proposed for the first time; namely, thin tablets of plaster of Paris made by casting sheets three-sixteenths of an inch thick on panes of glass and scratching them, before hardening, with ruled lines, so that when set they would readily break into oblongs measuring two and one-half by one and one-quarter inches. The pure white and highly polished surface of these tablets and its great power of condensing heated gases and exhibiting the true colors, their cheapness, thermal and hygroscopic properties of the tablets, the ease with which they may be prepared and carried, and the excellence of the results when the sublimed iodides, bromides, oxides and sulphides are deposited as coatings upon them, make them an ideal form of support in blowpipe work.

A small pit is made at one end of the tablet somewhat larger than a pin's head, and in this the ore to be tested is heated. The oxide coatings are produced by heating the substance *per se*, the bromides by adding to the substance a drop of fuming hydrobromic acid, and the iodides by adding a strong solution

of hydriodic acid (made by dissolving five ounces of metallic iodine in seven ounces of water, by passing a steady stream of hydrogen sulphide through the solution while the iodine is slowly added). All who have experimented with this solution will be ready to admit that it yields superb results, but though easily renewable when one is near a hydrogen sulphide generator it is very unstable, takes a long time to prepare and is troublesome to carry.

In 1890 Mr. F. A. Bowman read a paper before the Nova Scotia Natural History Society, in which was described a search for a solid reagent to replace the hydrogen iodide solution. He found that potassium hydrogen sulphide or any alkaline sulphate, which does not yield a coating of its own, mixed with potassium iodide would do very well. He also found that microcosmic salt and potassium iodide gave good results. This mixture is a favorite one with some blowpipe experts. Tin is the only metal in the three series of the periodic table, beginning with copper, silver and gold, which does not yield a characteristic coating with this reagent.

The writer has not been able to find whether there have been any other reagents besides these seriously proposed. Plaster of Paris as a support is mentioned in Moses and Parsons' late work as an alternative to charcoal. This is, as far as known to the writer, the only standard work, in which the colors of the films on the tablets are described.

In the rapid development of other methods in chemical work the blowpipe has fallen largely into disuse, and for many years, besides the work outlined above and that of Col. Ross and some valuable tests for individual elements proposed by Chapman, little or no advance has been made. There are two possible lines of future progress in blowpiping, one in the direction of increased power and simplicity, so as to make the method more valuable for the field work of the mineralogist, geologist and prospector, and the other in the direction of increased range and delicacy until the dry way tests rival the delicacy and distinctiveness of the wet tests, as they surpass them in expeditiousness. It may not be amiss, therefore, to call attention to the instrument of Plattner and Berzelius, which, in its mod-

ern form as the hot-blast blowpipe and with the new support and the new reagents and reactions now known to chemistry, is an instrument surpassed by the electric furnace only.

The cleanliness of the method here described, as compared with the charcoal method and the quickness with which sure results can be obtained with very small amounts, should call the blowpipe back to the table of the chemist for preliminary and confirmatory tests, to class work as an accompaniment of the wet methods, and to the lecture table for the purposes of illustration. It is possible to detect five or six metals in presence of each other on one tablet. Many of the coatings are permanent and are all renewable on reheating with addition of a drop of the reagent, so that a set of tablets carefully labelled with a pencil forms a permanent record of a set of experiments. The value of this to the practical chemist and to the student need not be emphasized. It may be noted that blowpiping is so much of an art that new methods are seldom well enough practiced, by those who have become skillful in other methods, to reveal their value.

The extensions of the plaster of Paris method here proposed are: A set of new reagents, which yield some new reactions which are of value in detecting elements in the presence of each other, notably gold and copper in very small amounts in the presence of all elements so far experimented with; arsenic, tin and antimony in presence of each other; sulphur in the presence of selenium and tellurium, and chlorine, bromine and iodine in the presence of each other; a new set of film tests which are found to be of great delicacy (the limits of delicacy are now being measured, it being found that gold, one part in one million, and copper, one part in four millions, are easily detectable); a change in the composition of the tablets which does away with the necessity for using platinum wire in the production of the colored glasses with borax and metaphosphoric acid, these being formed on the tablets with a decided gain in facility and delicacy; and lastly several new methods of handling the tablets themselves.

It is evident that solid reagents will always be the more convenient to carry afield, but, in the laboratory, liquids are to be preferred, since they are more readily applied, and when the

assay is heated, the reagent, which has soaked into the tablet, is fed steadily toward the hot portion of the tablet, so that the heated assay is constantly enveloped in the vapor of the reagent. For over two years the writer has used with satisfaction the following reagents, which have been selected from a score of experimental ones. They are stable and almost odorless, can be carried to the field in a solid form and so used if need be, while a few seconds suffice to prepare them in liquid form if it be desired so to use them.

The chief reagent is a saturated solution of iodine in a strong solution of potassium thiocyanate in water. The solution takes place almost instantly and with great absorption of heat. The bottleful now in use has been in use for over two years, a little of one or other of the ingredients being added from time to time as seemed to be required. Exact proportions are not necessary to the efficiency of the reagent. It can be prepared on the field from the solid chemicals at a moment's notice. The brilliancy of the iodide films produced with this solution are not one whit behind those possible with the pure solution of hydriodic acid. Its coatings tend to form in definite bands of color. The spheres of desposition of the iodide and the oxy-iodide are sometimes very well defined. Some striking and important variations are produced by the presence of the potassium thiocyanate, for example, with molybdenum, osmium, iridium, tin, antimony, lead, bismuth, cadmium and mercury.

Dr. Haanel showed in his second paper that by means of hydrobromic acid, copper and iron could be detected at one operation in the presence of each other and in the presence of nickel and cobalt and any other flux-coloring substances. Instead of the fuming acid with its dangerous properties, a mixture in molecular proportions of powdered potassium bromide and metaphosphoric acid, or potassium hydrogen phosphate or sulphate may be used. This, suggested by Bowman's work, suggests further a set of solid reagents, made by using potassium chloride, potassium fluoride and potassium iodide with metaphosphoric acid, and these form a valuable set for special tests. They have the advantage of yielding at once the colored flux and the coatings produced by any volatile matter in the assay.

When heated, the reaction represented by the following general equation takes place: $KX + HPO_3 = KPO_3 + HX$.

These two reagents, the iodine solution and the bromide mixture, suffice for the production of coatings. The following which are used to differentiate them, are dropped upon the oxide or iodide film and colored spots are produced, or the color is discharged to white (technically, *wiped*), or the coating disappears through solution and absorption by the tablet.

Dr. Haanel used ammonium hydroxide and yellow ammonium sulphide for the purpose of testing the solubility of the films and to produce the sulphide spots. Both of these are troublesome to carry, and the latter is objectionable on account of its intolerable odor, its instability and the fact that for its renewal the hydrogen sulphide generator is required. It has been found that a solution of potassium sulphide, strong enough to show a clear amber color, made by dissolving the solid potassium sulphide in water, or by boiling a strong solution of potassium hydroxide with an excess of flowers of sulphur till the solution assumes a blackish color, which on cooling will be amber yellow, fulfils all the required conditions. If through the action of light it is decomposed, all that is necessary for its renewal is to boil the solution and perhaps add a little sulphur. We therefore have a reagent which can be carried as a solid, can be renewed anywhere, is as efficient as the ammonium sulphide solution and is almost odorless.

In the place of ammonium hydroxide a solution of potassium cyanide is used, made a little more stable by the addition of a little ammonium or potassium hydroxide. Besides these the common acids of the laboratory are useful and a solution of potassium thiocyanate.

The potassium thiocyanate solution is used in two ways. It is either dropped on the coating to test its solubility and to note the colors produced after heating, or it is dropped on the tablet before the coating is deposited, and then the hot vapors sweeping over the moist spot, give with some metals characteristic reactions.

Those coatings which are pure white and therefore invisible on the white tablet, are examined on a tablet which has been

smoked in a flame, or on one streaked up the middle by means of a glass rod which has been dipped in a solution of boric and metaphosphoric acids mixed with lampblack or bone charcoal. In this way the coatings may be viewed on a white and on a black surface at the same time.

In order that the colored fluxes may be made on the tablets, the latter must be made more resistant to the dissolving effect of the metaphosphoric acid and the alkali in the borax. If one teaspoonful of boric acid be added to each quart of the water used in making the tablets, they will be found to be denser and to have the necessary quality. Borax can be fused on them without gathering any impurities from the plaster and if metaphosphoric acid be substituted for phosphor salt, we have a flux which will spread upon the tablet and exhibit the colors of all degrees of saturation at the same time. This reagent, first proposed by Ross, who described its reactions, is preferable to microcosmic salt, since, as it contains no volatile matter and melts readily to a clear glass, it will show by effervescence the presence of water or carbon dioxide, or other gas in a mineral. With cobalt it yields a fine violet when cold, which becomes blue on the addition of any of the alkali metals, for which therefore it furnishes a ready test. The only objection to this reagent is the tendency of the sticks to deliquesce, but a piece can be kept in a corked test-tube,[1] which can be readily dried over the flame, if dampness should gather. In dry weather it causes no trouble. Its solvent power is very great and the colors are fine. Ross asserts that silica and zirconia are the only oxides which are not soluble in this flux. The whole operation may be completed in the time usually required to form the bead in the platinum wire loop and the volatile oxide films will be found on the tablet above the glass, where they may be tested with potassium sulphide and the other reagents. One operation, therefore, suffices for the determination of the volatile acid elements, the volatile metal or metals, and flux-coloring metal. Metaphosphoric acid well replaces potassium hydrogen sulphate in the operation as

[1] In this laboratory each student is supplied with a set of very small dipping tubes and a wooden block into which holes are bored for the reception of a set of test-tubes closed with paraffined corks, to hold the reagents.

described in most text-books for the detection of carbon monoxide, carbon dioxide, iron, chlorine, bromine, iodine, nitrogen tetroxide, chlorine tetroxide, sulphur dioxide, hydrogen sulphide, hydrocyanic acid and acetic acid.

DESCRIPTIVE LIST OF REACTIONS OBTAINABLE ON THE TABLETS.

Copper *per se* yields with difficulty a coating of volatilized metal. With the iodine solution it yields a white iodide coating and an emerald green flame. The iodide treated with a drop of potassium sulphide gives with gentle heat a blackish gray, which is removed by greater heat. Potassium cyanide and nitric acid dissolve the sulphide; hydrochloric and sulphuric acids have no effect till heated and then they remove the spot. Potassium thiocyanate applied to the coating has no effect till heated, when a gray spot is shown. Any part of the coating touched with the tip of the flame shows the emerald green flame (Haanel). Metaphosphoric acid glass is greenish-blue when hot and a fine robin's egg blue when cold. Metaphosphoric acid and potassium bromide yield a splendid reddish violet coating of copper bromide (compare osmium). The bromide plus potassium sulphide shows a brown, which if heated turns blackish and then green, not affected by sulphuric acid, but immediately destroyed by a drop of nitric acid.

Copper plus metaphosphoric acid and potassium chloride yields a yellow brown cupric chloride, which, if treated with a drop of potassium thiocyanate, gives a black ring, which, if heated, becomes a black spot. If, before the assay is heated, a drop of nitric acid be placed one-half inch from the assay and a drop of potassium thiocyanate be placed above that, on heating a fine and very volatile blue-black coating is deposited far up the tablet. This blue-black is not affected by acetic acid, is wiped off by sulphuric acid slowly, and immediately by hydrochloric and nitric acid. The formula of this compound will be determined if some method be found, by which it may be collected in quantity. (See chlorine.)

Silver gives *per se* a pinkish gray coating, which touched by the blowpipe flame (flamed) becomes mottled brown. Reduced

globules are often shown. Metaphosphoric acid yields the same coating and a pearl-like glass. The iodine solution yields a pale yellow, paler when cold, and around the assay forms a black, which does not fuse into the tablet (compare lead). Flaming with oxidizing flame yields a mottled brown anywhere on the tablet. This is a very delicate test and as all other coatings are volatile, the flame drives them off and leaves the silver oxide. Potassium sulphide produces a spotted blackish brown, probably potassium silver sulphide, the analogue of ammonium silver oxide, for if treated with a drop of potassium cyanide it immediately disappears, but if it be first heated, the potassium cyanide has no effect. If only one-half of the sulphide spot be touched with the tip of the flame and then the potassium cyanide be applied, the untouched portion will disappear while the other half will remain. Potassium thiocyanate on the iodide wipes it off; when heated the spot turns black, which is not wiped off by potassium cyanide.

Gold is slightly volatile *per se* and more so if a solution of iodine in potassium iodide be used as a reagent, and the result is a fine rose-colored film of the metal. If potassium thiocyanate be present, no volatility is noticed. Gold and the other elements which respond to the new tests will be the subject of another paper.

Zinc *per se* yields a white coating, not very volatile and luminous yellow when hot. Potassium sulphide and potassium thiocyanate produce no visible change on zinc films. The iodide film is a white, which treated in any part with cobalt nitrate solution yields the well-known zincate of cobalt, which is quickly decomposed by a drop of nitric acid (compare tin). This reaction obtained in this way is decisive for zinc, as aluminum and silicon do not volatilize and are therefore not present in the coating. In the metaphosphoric acid glass, zinc causes flashes of light and detonations (Chapman). Metallic zinc sometimes yields *per se* a black sublimate along with the white oxide (compare arsenic.)

Cadmium *per se* yields one of the most beautiful of the oxide films, which consists of a rich brown with black farther away and somewhat iridescent near the assay. Acetic acid does not

affect it; potassium cyanide dissolves it at once (compare cadmium sulphide). Potassium sulphide and potassium thiocyanate yield a scarlet when hot, and bright yellow, cold. This cadmium sulphide is not affected by potassium cyanide, is quickly destroyed by nitric acid, less readily by hydrochloric acid, immediately by acetic acid (compare cadmium oxide), and is not affected by sulphuric acid (compare copper).

The iodide coating is white with well-defined borders, which is easily distinguished in the presence of other white coatings by the *per se* and sulphide reactions. In the assay and near it the sulphide reaction will be seen caused by the potassium thiocyanate in the iodine solution (see sulphur). In metaphosphoric acid cadmium acts like zinc and yields at the same time its oxide coating beyond the glass.

Mercury gives *per se* a very volatile film of mercury snow, which, with a feather, may be swept into a globule. It is not affected by the other reagents.

The iodide coating is a splendid combination of scarlet, yellow, and velvety green. This is caused by the mixing of the green mercurous iodide with the scarlet and yellow forms of the mercuric iodide. The reactions of each kind of iodide may be obtained on the one tablet. The green and the scarlet are the stable forms into which the coating changes on standing. A drop of the reagent or some more of the vapor blown across the coating changes all into the scarlet form. With mercurous iodide, sulphuric acid gives a yellow spot (mercurous sulphate). Potassium hydroxide gives a black; so does ammonium hydroxide, (iodomercurosamine, NH_2Hg_2I), and potassium sulphide. With the mercuric iodide, sulphuric acid increases the amount of the scarlet, potassium hydroxide yields a white, as does ammonium hydroxide (iodomercurosamine) and potassium sulphide, yield a white spot, quickly turning black. The sulphide spot, strange to say, is partially dissolved in nitric and hydrochloric acid, while sulphuric acid turns it brownish. Potassium cyanide yields a black and potassium thiocyanate a dark spot, and if heated both are wholly volatilized (compare lead, bismuth, and silver). Water has no effect on this coating (compare lead), nor

have hydrochloric, nitric, or sulphuric acids. By the last the coating is not readily wetted.

Gallium has not been experimented with. Indium yields a pale yellow iodide coating and a blue flame.

Thallium *per se* yields a feathery brown with white farther away and a green flame (compare arsenic and tellurium). Potassium sulphide gives a terra cotta brown spot with a black ring. Potassium cyanide and potassium thiocyanate have no effect upon it. The iodide film is an egg yellow with a purple black veil farther away. Potassium sulphide gives a rich brown which potassium cyanide darkens. Hydrochloric acid discharges it slowly and yellow is left (compare bismuth and tellurium). Potassium thiocyanate has no effect on the yellow or the black till heated, when it yields a white (compare bismuth, tellurium, tin, and lead). Potassium cyanide dissolves the black but has no effect on the yellow. Sulphuric acid has no effect. A drop of the reagent on the coating heated shows a spreading black and an orange ring.

Carbon yields a sooty coating, which comes better if sulphuric acid or metaphosphoric acid be used upon the assay. In the case of the carbonates, boric oxide or metaphosphoric acid yield an odorless effervescence (Ross, Chapman). Organic acids blacken the tablet when heated.

Silicon. An interesting reaction given by the silicates, especially the hydrous forms, is being investigated. Chapman dissolves a silicate in boric oxide and then precipitates the silica by adding metaphosphoric acid.

Germanium will give a light yellow iodide film, but none has been on hand to experiment with.

Tin gives a slightly volatile coating, showing a trace of brown when hot. Potassium thiocyanate, if dropped on the oxide and strongly heated gives a pale yellowish green, infusible (compare lead). The slight volatility of tin oxide suggests a scale of volatility, of great use in describing the formation of the films on the tablets. The scale runs in the order of increasing volatility: tin, zinc, cadmium, and mercury. Anything less volatile than tin might be classed as non-volatile.

The iodine solution yields a yellow, reddish brown when hot,

the brown fading instantly. Potassium sulphide yields a black with a brown edge, which darkens on heating. Potassium cyanide discharges the color, which turns black on heating, and when strongly heated shows the pale yellowish green (stannous thiocyanate, $Sn(SCN)_2$; compare lead, bismuth, arsenic, mercury and zinc). Water decomposes the film with formation of oxy-iodide.

Cobalt nitrate gives the bluish green, which is not so readily attacked by nitric acid as the zinc green.

Antimony tri- or pentachloride yields with all tin salts a fine purplish blue-black coating, stable in the presence of acids. Potassium thiocyanate decomposes it when heated and forms the pale green.

These tests with iodine, antimony trichloride, and with potassium thiocyanate remove tin from the list of metals determinable with difficulty before the blowpipe. They can be depended on through a wide range of mixtures.

Lead yields *per se* a white and yellow; reddish brown when hot. All lead salts fuse into the tablet with the formation of lead plumbate, one of the constituents of glass. Potassium sulphide produces a brownish black, with reddish brown ring.

The iodine solution gives a film which is chrome yellow, with a band of fainter yellow farther away (oxy-iodide?), and the assay is black. Potassium sulphide yields a spot with the reddish brown edge. Hydrochloric acid destroys the edge at once. Nitric acid wipes the spot off slowly, and sulphuric acid destroys the black and restores the yellow. The very volatile paler yellow on the outer edges is turned to a brighter color by the same treatment (compare mercury). Potassium cyanide produces a slight paleing of the sulphide color. Potassium thiocyanate on the iodide film gives a black ring, which heated becomes a black spot (compare bismuth). Water wipes off the coating (compare mercury, arsenic and silver).

The bromide film made by using potassium bromide and potassium hydrogen sulphate presents some interesting differences. It is white with a trace of yellow, the yellow fusing into the tablet. Potassium sulphide gives a spot, greenish for a moment and then black, on which potassium cyanide and potassium thiocyanate have no effect, but is partly destroyed by hydrochloric

acid, more rapidly by nitric acid, and completely by sulphuric acid. Potassium thiocyanate, placed on the sulphide and heated, gives a black ring; with greater heat, a yellow, and still greater heat, a greenish gray ring. Potassium cyanide on the iodide film has no effect till heated; then a white. Potassium thiocyanate has no effect on iodide till heated; then a yellowish spot appears (compare tin). The sulphide heated becomes grayish black, on which nitric acid and the other acids have no effect (compare copper).

It is a good illustration of Carnelley's law of color that in general the bromide film of any metal resembles the iodide film of an element either in a higher series in its own family or in the same series, in another family toward the left in the natural classification. Thus the bismuth bromide film resembles the iodide film of antimony and lead. Lead bromide resembles tin and thallium iodide. Thallium resembles mercury, and mercury resembles silver in the same way.

Nitrogen with metaphosphoric acid in the nitrates yields an effervescence with the fumes, odor and reactions of nitrogen tetroxide farther up the tablet, and in the cyanides, the odor of hydrocyanic acid. Nitrates with carbonaceous matter yield ammonia, which will cause white fumes to rise from a spot on the tablet moistened with hydrochloric acid. Ross reports that any nitrogen compound with boric oxide yields a tough transparent bead, and with metaphosphoric acid, purple in the reducing flame with manganese dioxide.

Vanadium gives with metaphosphoric acid a pale yellow in the oxidizing flame, and in the reducing flame a green. (Ross).

Phosphorus. A great desideratum in blowpipe analysis is a good test for this element and the phosphates.

Arsenic yields *per se* a brownish black with a white film falling farther away with odor of garlic and blue flame (compare thallium and tellurium). The iodide coat is white and pale yellow; the assay wholly volatile. Potassium sulphide, with a drop of hydrochloric acid, forms the yellow sulphide, little affected by acids. If oxalic acid be applied to a sulphide spot and then hydrochloric acid, no effect is noticeable. The yellow will show up still better next day (compare antimony). If a drop

of potassium thiocyanate be placed on the tablet about one inch above the assay, and between them a drop of nitric acid and the arsenical vapor be blown over them from the assay, there will generally be formed in the edge of the potassium thiocyanate spot a bright bluish green of unknown composition. All common acids except acetic destroy it. It shows well in the presence of salts of tin and antimony. When it does appear it is decisive for arsenic. This iodide film exhibits a very marked repulsive power for water, probably due to the arsenic oxide which forms with it. Potassium iodide with metaphosphoric acid yields more of the yellow than does the iodine solution.

Antimony *per se* yields a white and yellow band and white fumes. Potassium sulphide yields on this an orange brown, which is quickly destroyed by a drop of nitric acid.

The iodide film is a fine orange yellow far away with yellow nearer the assay and abundant white fumes. Potassium sulphide yields, especially when heated, an orange red with a rich brown and then a black beyond the spot. Hydrochloric acid slightly heated destroys it; nitric acid destroys it instantly; so also does its vapor. Potassium thiocyanate wipes the coating, but heated it yields a fine brown, which is permanent when exposed for months. Potassium cyanide wipes the coat. The orange yellow sulphide spot, produced on the iodide film obtained with potassium iodide and metaphosphoric acid, is not so susceptible to the action of nitric acid and is more rapidly destroyed by hydrochloric acid than the one described above.

If arsenic be present with antimony, there will be shown inside the yellowish orange of the iodide film, a fine peachy pink, which is hard to wet. Stannic chloride yields with antimony in most combinations a purplish blue-black, which is remarkably stable (Haanel). It is now being collected in quantity, with a view to the determination of its formula. It will be seen that with the blue with potassium thiocyanate, the rose pink, and the reactions of the sulphide with hydrochloric, nitric and oxalic acids, the presence of arsenic can be easily demonstrated in the presence of antimony and, as far as experiment has gone, in the presence of any other substances.

Bismuth yields *per se* a yellow ring near the assay and often a

brittle globule. Potassium sulphide gives on the white oxide a brownish black which nitric acid destroys and on which hydrochloric acid has little effect till heated, when it removes it completely. Sulphuric acid has no effect. Potassium thiocyanate on the oxide produces a yellow ring, and heated a yellow spot turning black. (It is to be noted that potassium thiocyanate itself when heated or treated with strong acids, shows on the tablet a fine yellow, which further heating renders colorless.)

The iodide film is a splendid combination of chocolate black, crimson and yellow, the assay turning black. Potassium sulphide forms a chocolate black, soluble in nitric acid and not effected by sulphuric acid. The latter acid on the iodide film produces a black and a dull red edge. This is probably the sulphide formed by the reduction of the acid by the decomposition products of the potassium thiocyanate, which fall with the iodides. It has been noticed, however, to happen with no other metal than bismuth. This reaction is very useful in detecting small quantities of bismuth in the presence of other metals giving dark colored films (compare tellurium). Potassium thiocyanate on the iodide wipes it off, forming a yellow ring, but when heated it forms a black spot with a brown ring. Potassium cyanide also wipes the iodide, but when heated forms a dark gray spot. Glacial acetic acid wipes off the yellow and the crimson, but has no effect on the chocolate iodide.

Sulphur. In looking for a better test for sulphur than the ordinary one with soda and a piece of silver, the stability at high temperatures and the two brilliant and characteristic colors of cadmium sulphide attracted attention, and the fact that it is easily formed in the presence of potassium cyanide. To a solution of cadmium bromide, potassium cyanide was added till precipitation took place and then the solution of the precipitate as potassium cadmium cyanide. This, dropped on a fragment of the sulphide and heated, will show on the tablet near the assay a brilliant scarlet when hot, and bright yellow when cold. This is not affected by potassium cyanide (compare cadmium oxide). One great advantage of this is that selenium and tellurium do not yield anything which can be confounded with these colors, selenium giving a grayish brown and tellurium a yellowish

brown. Sulphates may be reduced by potassium cyanide, or by glycerol. A sulphide or sulphate fused with potassium cyanide will, if touched with a drop of ferric chloride, show in the tablet the pinkish red of ferric thiocyanate. The sulphur in the tablet causes no trouble.

Selenium and tellurium are further differentiated from sulphur by their characteristic films, which are tests of great delicacy. Twenty-seven varieties of complex sulphides, such as bournonite, tetrahedrite, stannite, etc., and all of the common sulphides and sulphates, were found to respond to this test at once.

Selenium yields *per se* with characteristic odor and flame a fine reddish brown, almost pure red on the outer edges and black on the inner edges near the assay. Potassium cyanide wipes it off, while potassium thiocyanate has no effect, except that, if it be heated, a very stable red compound is formed (KSeCN ?).

The iodide film forms in color very similar to the *per se* coat, but more volatile. Potassium sulphide yields a yellow. Potassium cyanide wipes the iodide film off instantly, and therefore will reveal the presence of any other element not so affected, whose film might be hidden by the pronounced hues of the selenium film. Potassium thiocyanate has no effect, while it and heat wipe off most other coatings, and therefore will reveal the presence of selenium in obscuring associations, such as lead. Sulphuric acid shows a slight tendency to make this coating darker (compare bismuth).

Tellurium gives *per se* with flame and odor a brownish black with a white film falling nearer the assay (compare arsenic). Sulphuric acid, if gently heated, shows an effervescent pink of tellurium sulphate. Acetic acid wipes off this coat (compare cadmium). So do the potassium cyanide and ammonia fumes. The iodide film is brownish and purplish black, less brown than the *per se* coat. Potassium cyanide wipes it off in the cold. Potassium thiocyanate has no effect on the purple (compare thallium), and slightly dissolves the brown, and if nitric acid be added a yellow appears. Potassium sulphide darkens the coating a little. Sulphuric acid acts as on *per se* film.

Chromium yields an assay which is dark green when hot and

a fine green on cooling. This test can be made very delicate. Metaphosphoric acid gives similar colors.

Molybdenum yields *per se*, and especially by flaming, an ultramarine coating. The oxide film, which forms when the iodine solution is used, comes better by flaming of the film and in presence of vapors of sulphuric acid. A potassium thiocyanate spot, over which the vapors from the assay have swept, exhibits a splendid hyacinthine pink. Metaphosphoric and sulphuric acid vapors aid its formation. It is probably molybdenum thiocyanate ($Mo(SCN)_3$). If potassium thiocyanate be added to the assay this color will spread all around the edges of the blue, extending to a distance of two inches from the assay. This very delicate reaction is of special interest, from the fact that it shows that part of the potassium thiocyanate, or at least the radical thiocyanogen travels undecomposed that distance over the tablet and that all these films are formed in the presence of moist potassium thiocyanate or thiocyanogen vapors, which will account for the behavior of some of the films. This pink is decolorized by ammonia, not restored by nitric acid. Sulphuric acid dropped on the tablet will form a blue ring ($MoSO_4$). Metaphosphoric acid yields blue or bluish green glasses according to the degree of saturation (Ross).

Tungsten and uranium in metaphosphoric in the reducing flame yield, the former a blue and the latter a green glass (Ross).

Fluorine. If a fluoride be mixed with phosphoric acid and a piece of glass be laid on the tablet about two cm. away from the assay, a fine etched semicircle will show itself after the heating of the assay. The radius of the semicircle is about three cm. long.

Manganese yields with metaphosphoric acid a glass, which is violet hot and cold, colorless in the reducing flame, and turning green on the addition of an excess of soda (Chapman, Ross).

Chlorine. Chlorides, bromides and iodides of the alkali metals yield *per se* white coatings, which may be distinguished from other white coatings by their flames and by the action of a small quantity of the coating scraped together and mixed with the

metaphosphoric acid cobalt glass, which will remain blue on cooling.

A compound of chlorine if mixed with metaphosphoric acid and heated, in the reducing flame (if oxy salt), will cause white fumes to rise from a spot moistened with ammonia situated about two cm. above the assay. If a copper salt be present in the glass or near it, so that copper chloride vapors are formed and these are allowed to sweep over a spot of nitric acid and then over one of potassium thiocyanate, near the assay a yellowish brown coating of cupric chloride will form with an azure blue flame, and beyond the potassium thiocyanate spot a fine blue-black, very volatile (see copper).

A bromide with potassium cyanide added to it and the fused mass laid upon a copper glass and a drop of nitric acid added, a fine red will show itself. Bromides with metaphosphoric acid saturated with copper, upon blowing, yield a fine and very volatile reddish violet coating. If a bismuth salt be exposed to the hot vapors, it will yield a yellow coating. The spot on the tablet moistened with starch paste, not too near the assay, will turn yellow.

Similarly treated iodine compounds yield violet vapors, a violet in the glass appearing with effervescence, and with copper salt they yield a white coating, with bismuth scarlet and chocolate, and with starch a bluish black.

Iron gives an iodide film too delicate in color to show up well, either on the white or the black surface. Its presence can be shown by a red coloration after blowing hydrochloric acid vapors over the tablet, to turn all ferrous compounds into ferric, and then adding a drop of potassium thiocyanate to the coating. It is difficult to obtain plaster of Paris sufficiently pure not to give this reaction for iron. Such reaction can, however, be readily distinguished from that given by an assay. Metaphosphoric acid gives a luminous yellow when hot, which is perfectly colorless when cold. A drop of acid on this to produce ferric compounds, followed by a drop of potassium thiocyanate, will show the red of ferric thiocyanate, which is decolorized by phosphoric acid, but not by hydrochloric acid. Made in this way, this test is not too delicate to show the iron of composition. An assay of

iron treated with a drop of sulphuric acid and heated will show on the tablet a film of Venetian red.

Cobalt yields a glass blue hot, and violet cold; permanently blue if alkali be present. Boron trioxide acts similarly. With the iodine solution a spot around the assay turns pink, then deep blue on heating, and then black.

Nickel with boron trioxide separates as green fragments, which may be gathered by solution of the glass in water, and then the separated nickel (as any nickel compound) will yield in metaphosphoric acid, a reddish brown when hot and amber yellow when cold (Ross).

Palladium gives a dull blue-black film with the iodine solution, which is very characteristic. The assay turns dull black.

Osmium yields *per se* a greenish black. The iodide film is a combination of olive green, dove and slate colors, with red appearing around the lower edges. The edge of the coating nearest the assay shows greenish brown and the assay itself will be closely surrounded with an iridescent black film. Potassium sulphide turns the coating somewhat darker, which heated, becomes a brownish film, which is wiped off by hydrochloric and nitric acids and not affected by sulphuric acid and potassium cyanide. On the iodide films sulphuric acid has no effect; potassium thiocyanate has none till heated and then it turns brown. Hydrochloric and nitric acids remove the film. Potassium thiocyanate dropped on the tablet over an inch from the assay before the coating is deposited, will, when the vapors sweep over it, turn to a fine brick red, destroyed by potassium cyanide and the acids.

Potassium bromide and potassium hydrogen sulphate give a pinkish brown (compare copper). Potassium sulphide produces a gray not affected, which turns darker on being heated, destroyed by acids, and not affected by potassium cyanide.

Iridium yields with the iodide solution an indistinct brownish yellow coating and a potassium thiocyanate spot which in tint resembles the molybdenum spot, but it is covered with dots of darker pink.

Platinum gives an infusible gray film. Ruthenium and rhodium are being investigated.

All these reactions have been obtained from a large number of the compounds of each element except in the cases of osmium, indium and iridium. The writer will be glad to hear of any cases in which they fail and to receive specimens of combinations which cannot be unlocked by this method. One gram weight of any alloy is sufficient. The next work to be undertaken is to exhaustively determine the lowest percentage of any metal which can be determined with certainty in the presence of one, two, or any number of other metals, to describe the characteristic effect that one metal has on the coating yielded by another when they are deposited together and to determine the value of each metal as an interfering element.

COVERED TABLETS.

The tablets are easily cut with a knife and therefore they can be used in various ways. Open tube work can be performed on a tablet, if a groove be cut lengthwise of a tablet and laid upon another, groove down. A small pit for the assay is cut in the lower one about one centimeter from the end. The groove is cut so that its narrowest part is just above the assay pit, and from that point to the lower end it flares into a half funnel form and into this the flame is blown. By regulating the size of the groove at its narrowest part the amount of air which will flow over the assay may be regulated. This method is of great use when very small quantities of precipitates are to be tested. For instance, five-tenths mg. of arsenious oxide gave in one experiment a narrow coating one-half inch long on each tablet. This gives ample opportunity for making confirmatory tests. Various reagents may be placed along the groove to be acted on by the vapors, gold leaf for mercury, potassium cadmium cyanide and lead acetate for hydrogen sulphide fumes, starch, bismuth and antimony solutions for iodine, copper sulphate for chlorine, etc.

If a coating be made, or a small piece of volatile salt be placed in a small pit in the tablet and a thin tablet be placed over it, it is found that if potassium sulphide, or potassium thiocyanate be dropped on the upper tablet and the flame be directed upon the drop, they will pass through the tablet and reactions will take place away from the air. After a few seconds blowing the upper tablet will be found to be floating on a layer of hot

gas, which flows between the two smooth surfaces. Tin and arsenic, and other substances easily oxidizing in the air, form their sulphides very readily under these conditions. Potassium thiocyanate forms sulphides. It is in this way possible, by using ammonium hydroxide or hydrochloric acid, to form the sulphides in the presence of moist acid or alkaline vapors.

Other methods of using the tablets will be described later.

In teaching research methods, the plaster of Paris method is one of the finest instruments to use with beginners. In the course of an hour a student will have been able to make from twenty to forty different tests and without any delay in preparing solutions, or in waiting for filtration to take place, he will have produced the oxide, sulphide, chloride, bromide, and iodide of a given metal, and will have noted their colors, manner of deposition, volatility, solubility in several reagents, and the behavior of the assay itself at high temperatures and will have ransacked his vocabulary to find terms to describe the phenomena in his written notes. His skill in manipulation and his powers of observation are kept in liveliest exercise and his independence developed, for it is quite possible to give each student in a large class his own problem. In no other laboratory work do the compelled acts of judgment follow each other as rapidly. There are many problems which may be set requiring reference to standard chemical literature, and many simple and some very difficult equations of reactions to be written.

Not the least valuable consideration from an educational standpoint, is the aesthetic quality of the work. All the coatings are symmetrical in form and beautiful in shading, and many of them in brilliancy of hue and in delicacy of shading, rival the most splendid colors of flowers. This gives added interest to the work and is of great value since adult students are so frequently found to be greatly deficient in the color-sense, as children are not. There has not been opportunity to compare the shades of these films with the descriptions given in the Standard Dictionary. When this has been done, exact training can be given in color language also.

Apology is offered for publishing the results of this research at this stage, when so many unsolved problems stand along its

path, but this much is given in order that the practical value of these reactions and methods may be put to the test.

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AN ANALYTICAL INVESTIGATION OF THE HYDROLYSIS OF STARCH BY ACIDS.

BY GEO. W. ROLFE AND GEO. DEFREN.

Received July 3, 1896.

FEW problems of commercial analysis have been so complicated and so discouraging as that of the determination of the components of starch conversion products. The well-known schemes of commercial analysis of worts and similar products of the action of diastase are based on the assumption that but two simple compounds are formed from the starch—maltose and dextrin. In the case of glucose syrups and starch sugars, which are the results of acid hydrolysis, it is known that the reaction proceeds farther as dextrose is formed from the maltose and dextrin.

Musculus and Gruber[1] decided that these reactions went on together so that except at the very beginning or final stage of hydrolysis all of these compounds must be present in solution.

The analysis of acid-converted starch products must therefore take into consideration the presence of the third compound, dextrose.

Much doubt, however, has been thrown on the accuracy of such analyses, as during the past twenty years the researches of O'Sullivan, Brown, Heron, Morris, Bondonneau, Herzfeld, Musculus, Bruckner, Fischer, and other distinguished investigators, have shown that not only the simple compounds referred to can be isolated from starch products but also many others of quite distinct optical and chemical properties. Space will not permit a review of this work, which is in many points conflicting. The recent conclusion of Lintner and Düll is that the following compounds result from hydrolysis:[2]

1 *Bull. Soc. Chim.*, 2, 30.

2 *Ber. d. chem. Ges.*, 28, 1522–1531.

Hydrolysis with oxalic acid.	With diastase.
Amylodextrin	Amylodextrin
Erythrodextrin I	Erythrodextrin I
" IIα	......
" IIβ	......
Achroodextrin I	Achroodextrin I
" II	" II
Isomaltose	Isomaltose
Dextrose	Maltose

Others, as Brown and Morris,[1] deny the existence of the isomaltose of Fischer and Lintner and Düll, and mention another compound, maltodextrin, an intermediate between dextrin and maltose.

In 1885 Brown and Morris[2] discovered the remarkable law that at any stage of the conversion of starch by diastase, the total product, in its optical properties and relation to Fehling solution, behaved exactly as if made up of two components only, maltose and dextrin, so that it was possible by taking the rotatory power to calculate at once the cupric reducing power if the total carbohydrates were known. This law indicated that, however complicated the bodies isolated, they could be considered as existing in solution as two simple compounds, and did much to establish the validity of the principles of the usual commercial analyses of beer-worts and similar products.

The method of analysis of glucose syrups and starch sugars implies the assumption of a similar law, but the proof that this law actually exists under varying conditions of hydrolysis apparently has not been worked out.[3]

Our investigations have been made, first, to determine whether there was any simple constant relation between the optical rotation and the cupric reducing powers of starch products hydrolyzed under different conditions; and, secondly, whether any laws could be found affecting the three simple bodies assumed to be formed and determined by the usual methods of analysis.

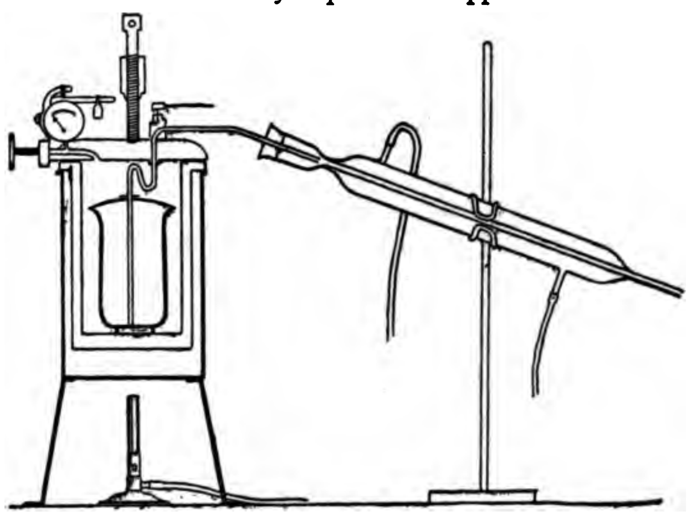
Incidentally we have collected some data as to the speed of hydrolysis, influence of carbohydrates on specific gravity of

[1] *J. Chem. Soc.*, No. 393. Aug., 1895.
[2] *Ann. Chem.* (Liebig), 231, 131.
[3] A very complete bibliography of the original publications on the carbohydrates is in *Tollen's Handbuch der Kohlenhydrate*, Vol. I, *1888*, 331–360; Vol. II, *1895*, 368–398.

solutions, and some looking to the adoption of a more rapid and accurate method of determining cupric reducing power by Fehling solution.

The latter data are included in a separate paper. The work on specific gravities is not yet sufficiently complete for publication.

An autoclave of the usual construction was modified in the following manner: The thermometer tube was taken out and in its place was attached a specially constructed valve, by means of which liquor cooking in a beaker in the interior could be removed at any time during the progress of the experiment. This superheated liquor was prevented from vaporizing by passing through a condenser. Excessive condensation into the beaker was prevented in large part by a well fitting lead cap. The illustration sufficiently explains the apparatus.



In most of the work about 100 grams of a good quality of commercial corn starch[1] was mixed with a liter of water con-

[1] An analysis of this starch by the usual commercial methods gave:

	Per cent.
Starch	89.15
Oil	0.14
Ash	0.12
Albuminoid	0.42
Water	10.21
	100.04

taining the hydrolyzing acid. Samples of from fifty to seventy-five cc. of the liquor were removed at different stages of the conversion and immediately shaken up with a few grams of marble dust. Two drops of tenth normal sodium hydroxide solution were then added to the sample, which was cooled and filtered. This method of neutralization, except in cases of very low converted samples, gave an absolutely clear filtrate, the filtration being exceedingly rapid, and the removal of the albuminoids being practically complete. Low-converted products often required to be heated with aluminum hydroxide before filtering.

The samples were tested as follows:

(1) For specific gravity by Westphal Balance, corrected to a temperature of 15.5° C.

(2) Specific rotatory power ($[\alpha]_D$) by a Schmidt and Haensch half-shade saccharimeter.

(3) Cupric reducing power by means of Fehling solution.

Total Solids—Total solids were calculated from the specific gravity of the solution by the factor 0.00386, which was taken to represent the influence of one gram of the mixed carbohydrates in 100 cc. of solution. Corrections were made when necessary for the influence of other substances in solution, not carbohydrates. This factor 386 is practically that of Balling and Brix and has been found exact for approximately ten per cent. solutions of cane sugar, and the balance of evidence seems to be that it is correct for starch products.

We have made several determinations of this factor by drying ten cc. of solution on rolls of dried paper at a temperature of 100–105° C. Our results point to the constancy of this factor 386 even in solutions of low rotatory power, but are not yet complete enough to establish the value for all rotations.

Therefore, in this work we have adopted the expedient used by Brown and Morris, and others, and calculated all optical and copper reduction constants on the assumption that all three carbohydrates in solution affect the specific gravity like cane sugar when the concentration is approximately ten per cent. Even if subsequent investigations show that this view is not exactly correct, the relative values of the constant will not be appreciably affected nor the truth of the laws as set forth.

To illustrate this method of calculation of constants we give the following from our own determinations:

Ten grams of dextrose dissolved in 100 cc. of water gave a rotation of 30.70° on the Schmidt and Haensch saccharimeter. This gives $[\alpha]_D$ as 52.8.[1] As the increase in specific gravity per gram of crystallized dextrose in 100 cc. is 0.00381, $[\alpha]_{D386}$ is 53.5.

9.751 grams of crystallized maltose anhydride in 100 cc. of water gave a rotation of 76.40. This gives an absolute specific rotatory power of 136.6. The specific gravity factor of maltose being 0.00390, $[\alpha]_{D386}$ is 135.2°. No exact figure is known for the influence of crystallized dextrin on the specific gravity of its solution. O'Sullivan gives 0.00385, and the balance of evidence seems to favor this. Hence 195 is probably correct for $[\alpha]_{D386}$.[2]

In like manner the values for K have been reduced to a dextrose with the factor 386.

Specific Rotatory Power.—All readings were made as nearly as possible at a temperature of 20° C. in 200 mm. tubes, the mean of several readings being taken. Corrections for zero-error were made frequently, and the instrument was carefully screened by glass plates from the heat of the lamps. Comparisons were made with a Laurent polariscope to determine the value of the division in terms of angular degrees for sodium light, the accuracy of the quartz wedges having being verified previously. With standard quartz plates the usual factor 0.346 was obtained, but solutions of commercial glucose of approximately ten per cent. gave the figure 0.344, which agrees with the recent work of Rimbach[3] and other investigators. We have taken, therefore, the latter factor in our calculation.

1 Precautions against bi-rotation were taken in both examples cited.

2 Brown and Hearn: *Ann. Chem.* (Liebig), 199, 190–243.

3 *Ber. d. chem. Ges.*, 27, 2282.

TABLE A.

COMPARISON OF SCHMIDT AND HAENSCH HALF-SHADE SACCHARIMETER WITH THAT OF LAURENT POLARISCOPE READING IN ANGULAR DEGREES.

Test.	S. and H. saccharimeter. (Using bat-wing burner and lens.) Reading.	Zero error.	Corrected reading.	Laurent polariscope. (Sodium flame.) Reading.	Zero error.	Corrected reading.	Factor.
(t = 20—22)							
Quartz A	62.965	0.300	62.665	21° 40′	0	21.666°	0.3457
"	62.800	0.150	62.650	21° 40′	0	21.666°	0.3458
"	62.970	0.290	62.680	21° 40.2′	0.6′	21.660°	0.3458
"	62.836	0.130	62.706	21° 40.7′	0.6′	21.666°	0.3455
Glucose A...	77.510	0.277	77.233	26° 35′	0	26.582°	0.3442
" B ...	76.355	0.150	76.205	26° 15.3′	0	26.254°	0.3445
" B ...	76.355	0.150	76.205	26° 14′	0	26.233°	0.3442
" C ...	76.535	0.150	76.385	26° 18′	0	26.300°	0.3443
" D ...	76.110	0.130	75.980	26° 10.3′	0.6′	26.162°	0.3443
(t = 25)							
Hydrolized starch products E.	92.73[1]	00	92.73	31° 56′	—1′	31.95°	0.3445
Hydrolized starch products F.	24.84	00	24.84	8° 32′	—1′	8.55°	0.3442

Cupric Reducing Power.—Our method is practically that of O'Sullivan, first published in 1876. The copper is weighed as the oxide. We have found this method exact and rapid. An analytical investigation of this process has been made by one of us and given in detail in a separate paper.

Plotted Results.—To show the relationship of the copper-reducing power, and the specific rotatory power of the products formed during the progress of the hydrolysis of the starch, we have plotted our results, taking as abscissae the decreasing values of the rotatory power, from the amylodextrin stage (195°) to that of dextrose ($[\alpha]_{D386} = 53.5°$), and as ordinates the cupric reducing power (K_{386}) taking that of an equivalent weight of dextrose as 100.[2] [See Plate A.]

1 Using Welsbach burner.

2 Data given in Table B.

TABLE B.

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes Cooking.	grams starch.	Atmospheric pressure.	Acid. Kind.		Acid. Amount cc.	Water cc.	Sp. gr. 15.5.	Sacch. reading.	Copper oxide.	$[\alpha]_D$ 386.	K 386.
8a	2	30	110	2	HCl	$\frac{n}{10}$	10	990	1.0456	98.0	0.1552	142.7	0.4747
	3	45							1.0394	59.3	0.2103	99.95	0.7480
	4	75							1.0374	41.5	0.2275	73.67	0.8537
	5	135							1.0367	32.9	0.2480	59.53	0.9283
10	1	15	110	2	HCl	$\frac{n}{10}$	10	990	1.0199	57.3	0.0060	191.30	0.0412
	2	45							1.0320	84.8	0.0366	176.0	0.1567
	3	75							1.0348	80.7	0.0923	154.0	0.3652
	4	100							1.0315	67.6	0.1026	142.5	0.4523
	5	130							1.0315	60.8	0.1258	128.1	0.5584
	6	160							1.0318	54.6	0.1368	114.0	0.5993
	7	190							1.0318	49.4	0.1594	103.1	0.6995
	8	220							1.0318	44.7	0.1781	93.95	0.7827
	9	250							1.0323	42.2	0.1848	86.66	0.8000
	10	280							1.0323	38.4	0.1940	78.94	0.8407
11	1	15	110	2	HCl	$\frac{n}{10}$	100	900	1.0414	89.55	0.1290	143.6	0.4434
	2	30							1.0417	55.95	0.2320	89.10	0.7825
	3	45							1.0419	41.0	0.2747	64.98	0.9230
	4	60							1.0414	36.0	0.2837	57.75	0.9663
	5	75							1.0412	33.0	0.2830	53.19	0.9685
	6	90							1.0406	32.5	0.2763	53.16	0.9590
13	1	15	110	2	HCl	$\frac{n}{10}$	100	900	1.0394	103.2	0.0056	174.0	0.1958
	2	45							1.0384	75.7	0.1500	129.9	0.5405
	3	60							1.0380	61.1	0.1898	105.7	0.6988
	4	90							1.0380	45.5	0.2339	79.50	0.8646
	5	120							1.0375		0.2448	67.75	0.9175
14	2	22½	110	2	HCl	$\frac{n}{10}$	100	900	1.0379	97.8	0.0661	167.4	0.2415
	3	35							1.0384	85.9	0.1095	148.6	0.3964
	4	52½							1.0370	64.75	0.1664	116.2	0.6279
	5	75							1.0374	50.80	0.2040	90.20	0.7640

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes cooking.	grams starch.	Atmospheric pressure.	Acid. Kind.		Amount cc.	Water cc.	Sp. gr. 15.5.	Sacch. reading	Copper oxide.	$[\alpha]_D$ 386.	K 386.
	6	105							1.0374	39.60	0.2281	70.31	0.8561
	7	135							1.0374	34.95	0.2493	62.34	0.9367
15	2	30	110	2	HCl	$\frac{n}{10}$	1000		1.0371	88.1	0.0890	157.7	0.3329
	3	60							1.0337	67.05	0.1247	132.1	0.5146
	4	90							1.0337	56.50	0.1551	111.4	0.6421
	5	120							1.0337	46.00	0.1863	90.65	0.7727
16	1	25	110	2	HCl	$\frac{n}{10}$	1000		1.0327	79.90	0.0679	162.3	0.2877
	2	40							1.0393	81.40	0.1395	137.5	0.4946
	3	50							1.0380	70.60	0.1617	123.4	0.5936
	4	75							1.0380	57.00	0.1994	99.61	0.7348
17	1	15	55	2	HCl	$\frac{n}{10}$	25	475	1.0360	105.5	0.0173	188.5	0.0643
	2	23							1.0341	92.9	0.0344	180.9	0.1393
	3	33							1.0343	88.1	0.0539	170.6	0.2173
	4	42							1.0352	86.2	0.0751	162.7	0.2963
	5	50							1.0308	79.5	0.0828	157.0	0.3396
18	1	75	60	2	HCl	$\frac{n}{10}$	50	450	1.0422	74.7	0.1892	117.6	0.6273
	2	90							1.0423	68.0	0.2100	106.8	0.6958
	3	110							1.0428	60.3	0.2369	93.56	0.7796
	4	120							1.0428	52.6	0.2587	81.62	0.8507
	5	135							1.0429	49.2	0.2676	76.05	0.8720
19	1	15	60	2	HCl	$\frac{n}{10}$	50	450	1.0383	105.0	0.0329	182.1	0.1186
	2	30							1.0374	87.0	0.0975	154.5	0.3619
	3	40							1.0374	66.2	0.1337	117.6	0.6255
	4	130							1.0359	39.8	0.2272	73.62	0.8882
	5	150							1.0326	34.8	0.2093	70.89	0.8997
20	1	45	60	2	$H_2C_2O_4$	$\frac{n}{10}$	50	450	1.0327	87.2	0.0396	177.1	0.1673
	2	90							1.0301	71.2	0.0766	157.7	0.3526
	3	120							1.0318	65.8	0.1125	135.5	0.4917
21	2	60	60	2	$H_2C_2O_4$	$\frac{n}{10}$	100	400	1.0352	75.9	0.1145	143.2	0.4523

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes cooking.	grams starch.	Atmospheric pressure.	Acid. Kind.	Acid.	Amount cc.	Water cc.	Sp. gr. 15.5.	Sacch. reading	Copper oxide.	$[\alpha]_D$ 386.	K 386.
	3	75							1.0359	71.6	0.1350	132.4	0.5237
	4	105							1.0355	64.0	0.1577	119.8	0.6200
24	1	30	65	2	HCl	$\frac{n}{10}$	100	400	1.0440	88.2	0.1651	133.1	0.5236
	3	60							1.0371	38.1	2x(0.1211)	68.19	0.9080
	4	75							1.0376	33.95	2x(0.1319)	59.95	0.9745
	5	90							1.0406	34.7	2x(0.1388)	56.75	0.9526
25	1	45	65	2	$H_2C_2O_4$	$\frac{n}{10}$	200	300	1.0414	99.7	0.0966	159.9	0.3240
	2	90							1.0448	85.6	0.1799	126.9	0.5611
	3	135							1.0452	67.0	2x(0.1265)	98.42	0.7791
	4	180							1.0458	55.3	2x(0.1401)	80.17	0.8525
	5	225							1.0455	47.7	2x(0.1483)	69.61	0.9088
26	1	30	65	2	H_2SO_4	$\frac{n}{10}$	100	400	1.0447	110.9	0.0869	164.7	0.2760
	2	62							1.0466	89.3	2x(0.0821)	127.3	0.5480
	3	90							1.0478	74.2	2x(0.1227)	103.[illegible]	0.7144
	4	120							1.0500	63.1	2x(0.1475)	83.79	0.8206
	5	150							1.0525	56.4	2x(0.1614)	70.96	0.8848
27	1	10	60	4	HCl	$\frac{n}{10}$	50	450	1.0430	95.2	0.1281	147.0	0.4144
	2	20							1.0430	60.85	2x(0.1196)	93.97	0.7738
	3	30							1.0430	42.7	2x(0.1414)	65.94	0.9162
	4	45							1.0430	35.3	2x(0.1466)	54.51	0.9506
	5	60							1.0430	34.8	2x(0.1533)	53.70	0.9968
33	1	10	60	4	HCl	$\frac{n}{10}$	100	400	1.0426	60.8	0.2351	94.77	0.7754
	2	15							1.0426	41.4	0.2833	64.54	0.9378
	3	20							1.0423	35.4	0.2919	55.58	0.9736
34	1	10	60	3	HCl	$\frac{n}{10}$	200	300	1.0435	56.4	0.2532	86.10	0.8143
35	1	90	60	1	HCl	$\frac{n}{10}$	100	400	1.0381	87.6	0.0992	152.7	0.3616
	2	180							1.0391	66.5	0.1887	112.9	0.6751
	3	225							1.0403	49.5	0.2525	81.56	0.8831
39	2	90	60	4	HCl	$\frac{n}{10}$	50	450	1.0384	39.7	0.2621	53.01	0.9607
	3	120							1.0378	30.4	0.2628	53.40	0.9779

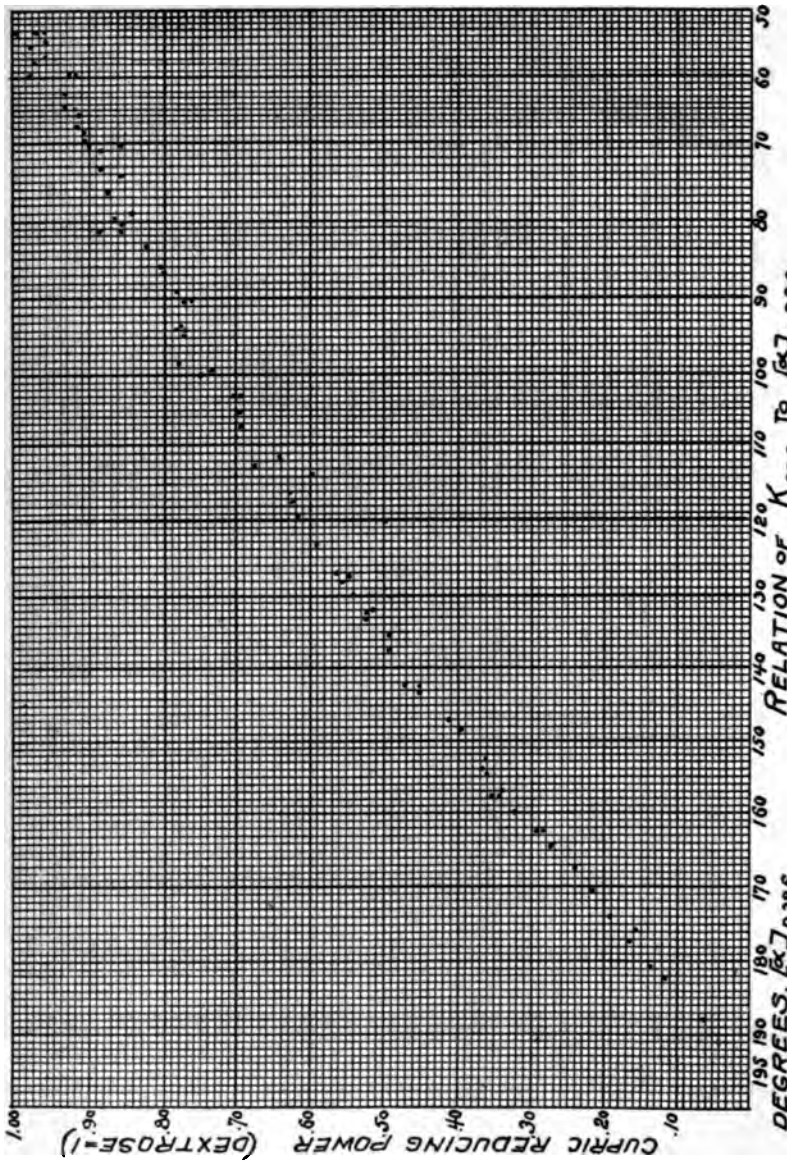

RELATION OF K_{386} TO $[\alpha]_{D386}$
DEGREES. $[\alpha]_{D386}$
CUPRIC REDUCING POWER (DEXTROSE=1)

PLATE A.

The results point to the remarkable fact that the cupric reducing power of the total product bears a constant relation to the specific rotatory power, even when the starch is hydrolyzed under widely varying conditions. Hence, given the one, the value of the other can be calculated. To a rotation of about 90°, the plotted results outline with extraordinary exactness the arc of a circle, the equation of which is

$$x^2 + y^2 + 468x - 646y + 1580 = 0,$$

which exactly intercepts the "zero" and "hundred" points at 195 and 53.5, respectively. The upper part of the curve is not so well defined, the results showing more discrepancy at the high conversion stages. This may be due to some decomposition and the formation of "reversion" products as stated by Wohl,[1] Maercker, Ost, and others. Wohl's figures show the maximum amount of dextrose possible to be 92.7 per cent. of the theoretical quantity. Others give ninety-six to ninety-seven per cent., the missing dextrose being supposed to be converted into dextrin-like bodies identical with those variously described as "gallisin," "isomaltose," etc. We have experimented but little along this line, having made but one hydrolysis with this special object, using $\frac{N}{100}$ hydrochloric acid at four atmospheres pressure, with the following results:

Time of cooking.	$[\alpha]_D$.
60 minutes	55.24
90 "	53.09
120 "	53.40
150 "	54.42

While several of our own results at the low rotations show a cupric reducing power of only about ninety-six per cent. of that of pure dextrose, we do not think that we are justified in arriving at any definite conclusion with the data at hand.

That the solutions begin to color considerably at rotations beyond 90° is, moreover, a strong indication of such decomposition. On the other hand, this accounts for much of the discrepancy of the plot at this part of the curve, as it is exceedingly difficult to get accurate readings on the saccharimeter of these highly colored solutions. Obviously, too, slight errors in the

[1] *Ber. d. chem. Ges.*, 23, 2101.

readings affect the calculations of the rotatory power the most at these lowest rotations.

Quite as noteworthy are the curves[1] plotted by taking the values of maltose, dextrin, and dextrose as computed for every

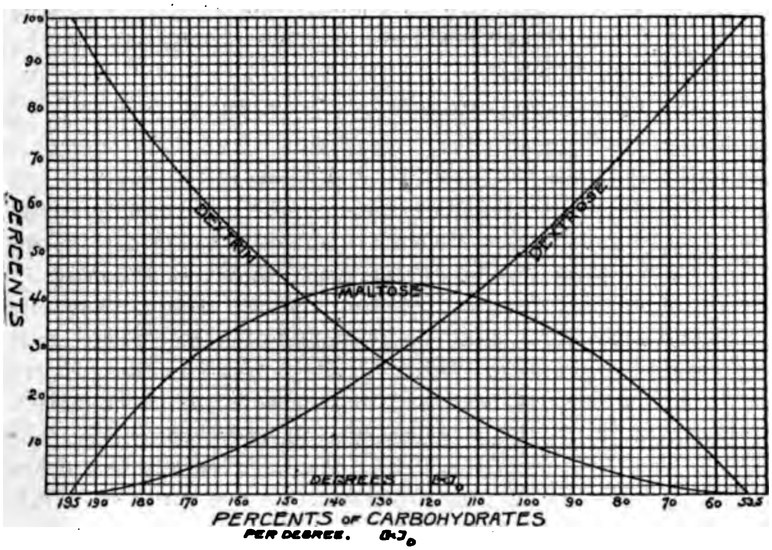


PLATE B.

five degrees of rotation from the values of K, as given by this curve.

In this work we have figured constants for solids estimated from the specific gravities of solutions by the factor, 386, and calculated percentages by the well-known equations:

$$g + m + d = 1.00$$
$$g + 0.61m = K$$
$$195d + 135.2m + 53.5g = \alpha$$

Where g is per cent. dextrose,
m is per cent. maltose,
and d is per cent. dextrin.

$$\text{Hence, } m = \frac{d + 141.5K - 195}{27.82}$$

[1] See plate B.

Examining these curves we see that the dextrin starting from the maximum of 100 per cent. gradually falls to zero near the rotation corresponding to dextrose, while the maltose gradually rises, reaches a maximum percentage of 44.1 at about 129° rotation, corresponding to the usual state of conversion of commercial glucose, and then falls, disappearing at 53.5°. The dextrose, on the contrary, steadily mounts to 100 per cent. It will be noted, too, that at the point of maximum maltose the dextrin and dextrose, as shown by the intersection of the curves, are present in equal quantity.

Tests with phenylhydrazin acetate show the presence of the dextrose distinctly at about 185°, and we had hoped to prove the gradual rise of the dextrose percentage by means of the dextrosazon. While copious precipitates of this beautiful compound were obtained, any attempt of ours to isolate it in anything like quantitative amounts proved a failure, even in solutions containing a known amount of pure dextrose. We hope to take this up more fully in a later investigation.

We have also calculated a table (Table C) from the curves giving the value of maltose, dextrose, and dextrin within one-tenth per cent. for successive stages of acid hydrolysis represented by each degree of rotation between 195 and 53.5. This table, calculated for the factor 386, makes no allowance for possible decomposition of high-converted products.

TABLE C.

CALCULATED VALUES OF CUPRIC REDUCING POWERS AND PARTS OF MALTOSE, DEXTROSE AND DEXTRIN PER UNIT OF CARBOHYDRATE FOR EACH DEGREE OF ROTATION OF A NORMALLY HYDROLYZED STARCH SOLUTION.

$[\alpha]^{20°}_{D\ 386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
195	0.000	0.000	0.000	1.000
194	0.011	0.017	0.001	0.982
193	0.022	0.033	0.001	0.966
192	0.032	0.048	0.002	0.950
191	0.041	0.063	0.002	0.935
190	0.051	0.079	0.003	0.918
189	0.061	0.094	0.004	0.902
188	0.071	0.110	0.005	0.885
187	0.081	0.123	0.007	0.870

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
186	0.090	0.135	0.009	0.856
185	0.100	0.147	0.010	0.843
184	0.109	0.160	0.013	0.827
183	0.118	0.171	0.016	0.813
182	0.127	0.182	0.019	0.799
181	0.137	0.192	0.022	0.786
180	0.146	0.203	0.025	0.772
179	0.155	0.212	0.028	0.760
178	0.164	0.222	0.031	0.747
177	0.173	0.231	0.034	0.735
176	0.182	0.240	0.037	0.723
175	0.191	0.250	0.040	0.710
174	0.199	0.257	0.043	0.700
173	0.207	0.265	0.047	0.688
172	0.216	0.273	0.050	0.677
171	0.224	0.280	0.054	0.666
170	0.233	0.287	0.058	0.655
169	0.242	0.294	0.062	0.644
168	0.251	0.301	0.066	0.633
167	0.259	0.307	0.071	0.622
166	0.267	0.314	0.075	0.611
165	0.275	0.320	0.080	0.600
164	0.283	0.326	0.084	0.590
163	0.292	0.332	0.089	0.579
162	0.300	0.338	0.093	0.569
161	0.308	0.344	0.098	0.558
160	0.316	0.349	0.103	0.548
159	0.324	0.356	0.107	0.537
158	0.332	0.362	0.111	0.527
157	0.340	0.369	0.115	0.516
156	0.348	0.373	0.121	0.506
155	0.356	0.378	0.126	0.496
154	0.365	0.383	0.130	0.487
153	0.373	0.388	0.135	0.477
152	0.381	0.392	0.141	0.467
151	0.389	0.397	0.146	0.457
150	0.397	0.401	0.153	0.446
149	0.404	0.405	0.157	0.438
148	0.412	0.408	0.163	0.429
147	0.419	0.412	0.164	0.420
146	0.427	0.415	0.174	0.411
145	0.435	0.415	0.182	0.403
144	0.442	0.421	0.186	0.393
143	0.450	0.423	0.192	0.385

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
142	0.458	0.425	0.199	0.376
141	0.465	0.427	0.205	0.368
140	0.473	0.428	0.212	0.360
139	0.481	0.431	0.217	0.352
138	0.488	0.432	0.224	0.344
137	0.496	0.434	0.231	0.335
136	0.503	0.436	0.237	0.327
135	0.510	0.437	0.243	0.320
134	0.517	0.438	0.249	0.313
133	0.524	0.439	0.256	0.305
132	0.531	0.439	0.263	0.298
131	0.538	0.440	0.270	0.290
130	0.546	0.440	0.277	0.283
129	0.553	0.441	0.284	0.275
128	0.560	0.441	0.291	0.268
127	0.567	0.440	0.298	0.262
126	0.574	0.440	0.305	0.255
125	0.580	0.439	0.313	0.248
124	0.588	0.438	0.320	0.242
123	0.595	0.438	0.327	0.235
122	0.602	0.437	0.335	0.228
121	0.608	0.436	0.343	0.221
120	0.614	0.435	0.350	0.215
119	0.621	0.433	0.358	0.209
118	0.628	0.431	0.366	0.203
117	0.635	0.429	0.374	0.197
116	0.642	0.428	0.381	0.191
115	0.649	0.425	0.390	0.185
114	0.656	0.422	0.398	0.180
113	0.663	0.420	0.408	0.174
112	0.669	0.417	0.414	0.169
111	0.675	0.414	0.423	0.164
110	0.681	0.408	0.432	0.160
109	0.687	0.407	0.439	0.154
108	0.694	0.403	0.448	0.149
107	0.700	0.400	0.456	0.144
106	0.707	0.396	0.465	0.139
105	0.713	0.392	0.474	0.134
104	0.719	0.387	0.483	0.130
103	0.725	0.383	0.492	0.125
102	0.732	0.379	0.500	0.121
101	0.738	0.375	0.508	0.117
100	0.744	0.370	0.518	0.112
99	0.750	0.366	0.527	0.107

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
98	0.757	0.361	0.537	0.102
97	0.763	0.356	0.546	0.098
96	0.769	0.350	0.556	0.094
95	0.775	0.345	0.565	0.090
94	0.781	0.341	0.574	0.085
93	0.787	0.336	0.583	0.081
92	0.793	0.331	0.592	0.077
91	0.799	0.326	0.601	0.073
90	0.805	0.320	0.610	0.070
89	0.810	0.314	0.620	0.066
88	0.816	0.308	0.629	0.063
87	0.822	0.302	0.638	0.060
86	0.828	0.295	0.649	0.056
85	0.834	0.288	0.658	0.054
84	0.839	0.282	0.667	0.051
83	0.844	0.275	0.677	0.048
82	0.850	0.267	0.688	0.045
81	0.856	0.259	0.698	0.043
80	0.862	0.251	0.709	0.040
79	0.867	0.243	0.719	0.038
78	0.872	0.234	0.730	0.036
77	0.878	0.225	0.741	0.034
76	0.884	0.217	0.751	0.032
75	0.889	0.208	0.762	0.030
74	0.895	0.200	0.772	0.028
73	0.901	0.191	0.783	0.026
72	0.906	0.182	0.794	0.024
71	0.911	0.173	0.805	0.022
70	0.916	0.163	0.817	0.020
69	0.921	0.153	0.828	0.019
68	0.926	0.143	0.839	0.018
67	0.932	0.134	0.850	0.016
66	0.937	0.125	0.861	0.014
65	0.942	0.115	0.872	0.013
64	0.947	0.105	0.883	0.012
63	0.952	0.095	0.895	0.010
62	0.957	0.085	0.906	0.009
61	0.962	0.075	0.917	0.008
60	0.967	0.065	0.927	0.008
59	0.972	0.055	0.938	0.007
58	0.977	0.045	0.949	0.006
57	0.982	0.035	0.960	0.005
56	0.987	0.025	0.971	0.004
55	0.992	0.015	0.982	0.003
54	0.997	0.005	0.993	0.002
53.5	1.000	0.000	1.000	0.000

It would seem obvious that we are now prepared to determine whether a sample of glucose is a product of one hydrolysis or is a mixture of two separately converted products, by comparison of the actual analytical results with those calculated from the rotatory power.

For testing this method we have made a few analyses of commercial glucoses obtained in open market.

In the manufacture of glucose syrup all the starch is not hydrolyzed under strictly the same conditions, as the factory practice is to pump the starch into the converter, which is under steam pressure and already contains the hydrolyzing acid. As the filling of a converter takes about one-third of the total time of cooking, it is clear that there is a radical difference in the time of hydrolysis of different portions of starch. Nevertheless, we have found that samples known to have been made under these conditions conform to the laws of our curve, and the evidence seems strong that those which depart widely from these conditions are mechanical mixtures.

The following determinations of four samples of commercial glucose giving the cupric reducing power as found and as calculated for the corresponding rotation will illustrate the method:

Sample.	α_{D386}.	K_{386} (obtained).	K_{386} (calculated).
I. C. Pope Co. (J)·····	131.1	0.566	0.537
II. C. Pope Co. (M)····	125.4	0.578	0.578
III. Rockford Co ·······	141.9	0.454	0.457
IV. Chicago Co·········	137.2	0.505	0.495

Evidently II and III are normally hydrolyzed. IV is possibly a mixture, while I is undoubtedly so. As this latter is a sample of jelly goods which in factory practice are often made by mixing two lots, our conclusion is strengthened.

From the results as a whole we have concluded that the evidence is strong, (1) that in any homogeneous acid-converted starch product, irrespective of the conditions of hydrolysis, the specific rotatory power always represents the same chemical composition.

(2) That but three simple carbohydrates,[1] possible in molecular aggregates, exist in the solution of a starch product hydrolyzed by acids.

[1] Leaving out of consideration the possible small amounts of products formed by reversion.

DETERMINATION OF THE CONVERSION OF COMMERCIAL GLUCOSE.

In the manufacture of glucose it is obviously essential to have a rapid means of determining the degree of conversion of the starch during the cooking process. The usual factory practice is to control the conversion by means of iodine color tests. These tests are usually made by adding a definite number of drops of standard iodine solution to a test-tube of the cooled glucose liquor. The tint at which the conversion is considered complete varies in general practice from that corresponding to $[\alpha]_D = 128$ to $[\alpha]_D = 135$, the variation being even greater in some cases, depending on the ideas of the manufacturer and the grade of goods desired.

By daily practice workmen become quite expert in making these iodine tints, which are usually carried out by crude methods and read off without comparison with any standard. Nevertheless, the product, when examined by more refined laboratory processes, shows wide variations from day to day, which does not appear surprising when we examine into the errors of such color tests.

Assuming that the test is carried out under uniform conditions of concentration and proportion of reagent to liquor to be tested, which is by no means always the case, the other conditions affecting the color are (1) temperature, (2) turbidity, and (3) illumination.

Uniform temperature can be obtained easily by some simple cooling device as a stream of running water.

The acid converter liquors are always turbid when tested, as filtration in this rapid testing is impracticable. The turbidity, however, is fairly constant. It is the third condition, that of illumination, which is constantly variable and which gives rise to the greatest error. This source of error can be largely eliminated by the use of a comparison standard, prepared of the same volume as that used in the color test and hermetically sealed in a glass tube of the standard size used in testing. Mixtures of solutions of iron salts with finely pulverized glass giving the requisite turbidity when shaken, can be easily made to exactly match the iodine tint, and will preserve their intensity indefi-

nitely. When properly adjusted by means of polariscopic tests such standards have served well to fix the point of conversion within narrow limits and have done much to insure a uniform product.

It is of course important that these should be in the hands of the chemist or superintendent of the works, a much more exact means of testing the degree of conversion. This is most naturally accomplished by determining the specific rotatory power.

We have arranged a table for quickly calculating specific rotatory power, and found it so useful that we venture to publish it. The following simple calculation will sufficiently explain the principles on which the table has been worked out:

TABLE D.

TABLE FOR DETERMINING SPECIFIC ROTATORY POWER OF SOLUTIONS OF 7.50°–10° BRIX BY READING OF VENTZKE SACCHARIMETER.

Brix.	Sp. gr.	W = gram per 100 cc.	Log $\frac{17.20}{W}$.	Brix.	Sp. gr.	W = gram per 100 cc.	Log $\left(\frac{17.20}{W}\right)$.
7.50	1.0298	7.724	0.3477	8.80	1.0352	9.110	0.2760
7.55	1.0300	7.777	0.3447	8.85	1.0354	9.163	0.2735
7.60	1.0302	7.829	0.3418	8.90	1.0356	9.217	0.2709
7.65	1.0304	7.883	0.3388	8.95	1.0358	9.270	0.2684
7.70	1.0306	7.936	0.3359	9.00	1.0360	9.324	0.2657
7.75	1.0308	7.989	0.3330	9.05	1.0362	9.378	0.2634
7.80	1.0310	8.042	0.3301	9.10	1.0364	9.430	0.2610
7.85	1.0312	8.096	0.3272	9.15	1.0366	9.484	0.2585
7.90	1.0315	8.149	0.3244	9.20	1.0368	9.538	0.2560
7.95	1.0317	8.202	0.3216	9.25	1.0370	9.592	0.2536
8.00	1.0319	8.255	0.3187	9.30	1.0372	9.646	0.2510
8.05	1.0321	8.308	0.3160	9.35	1.0374	9.690	0:2488
8.10	1.0323	8.361	0.3132	9.40	1.0376	9.753	0.2464
8.15	1.0325	0.415	0.3104	9.45	1.0378	9.807	0.2440
8.20	1.0327	8.468	0.3077	9.50	1.0381	9.862	0.2415
8.25	1.0329	8.522	0.3050	9.55	1.0383	9.916	0.2391
8.30	1.033:	8.575	0.3022	9.60	1.0385	9.970	0.2368
8.35	1.0333	8.629	0.2995	9.65	1.0387	10.023	0.2346
8.40	1.0335	8.682	0.2969	9.70	1.0389	10.077	0.2323
8.45	1.0337	8.735	0.2943	9.75	1.0391	10.130	0.2300
8.50	1.0339	8.788	0.2916	9.80	1.0393	10.185	0.2277
8.55	1.0341	8.842	0.2889	9.85	1.0395	10.239	0.2252
8.60	1 0343	8.895	0.2864	9.90	1.0397	10.293	0.2231
8.65	1.0345	8.949	0.2838	9.95	1.0399	10.347	0.2207
8.70	1.0347	9.002	0.2812	10.00	1.0401	10.401	0.2185
8.75	1.0350	9.056	0.2786				

Taking the usual formula for the specific rotatory power, $\alpha = \frac{av}{lw}$, where a is the angle of rotation of the solution of w

gram of the active substance in v cc. of water observed through a column l decimeters long. If we make $a = \alpha$ it is plain w is the weight of substance under standard conditions which will give a direct reading of the specific rotatory power without calculation. In an instrument reading in angular degrees under the usual conditions of $v = 100$ and $l = 2$, w is therefore 50 g.

If a is the reading of a saccharimeter with the Ventzke scale, $w = 50 \times 0.344 = 17.20$, and the specific rotatory power of any solution of known concentration of an optically active substance will be $\frac{17.2a}{w}$. The easiest way of finding the concentration of glucose solutions with sufficient exactness for this work is by the Brix (or Balling) hydrometer, as this instrument is now made of great accuracy.

Brix hydrometers are carried in regular stock of the larger houses dealing in chemical apparatus for brewers and sugar manufacturers, with scales having a range of about five degrees and easily read to 0.05 per cent. Thermometers are attached having corrections for temperature marked on the scale. Concentrations of about ten per cent. are most convenient for polarizing; hence a spindle will be needed reading from five to ten per cent.

The method of determining rotatory powers is as follows: The glucose is diluted to an approximately ten per cent. solution. An exact Brix (or Balling) reading is taken, corrected for standard temperature and the solution polarized in a 200 mm. tube in any saccharimeter with the Ventzke scale. The logarithm of the factor $\frac{17.20}{w}$ corresponding to the Brix reading is then found in the table. Therefore, the calculation which is, $\log\ [\alpha]_D = \log\ \left(\frac{17.20}{w}\right) + \log\ a$, simply requires finding the logarithm of the saccharimeter reading and the number corresponding to the sum of this and the logarithm given in the table. This number is the required specific rotatory power.[1]

[1] Obviously a table made on the scheme of the well-known Schmitz table for cane-sugar syrups would do away with all calculation. Such a table is, however, rather bulky for insertion here.

Thus a solution of 7.85 Brix having a reading of 51.7°, Ventzke has the rotatory power of its anhydrous carbohydrates determined as follows:

By the table, the corresponding logarithmic factor is 0.3272.

$$\begin{array}{ll} \text{Log } 51.7 = & 1.7135 \\ \text{Factor} & 0.3272 \\ \hline & 2.0407 = \log 109.8 \end{array}$$

which is the required rotatory power.

In this calculation no correction is made for ash, which, as a rule, does not affect the results appreciably.

The errors due to the slight variations in the concentration of the solutions used and changes in the temperature of the laboratory are too small to be taken into consideration in factory work or in general commercial analysis. The method in practice is quite as rapid as the "quotient of purity" determination of cane-sugar syrups. We suggest that this, or some similar scheme, be uniformly used for expressing the results of all polarimetric investigations of honeys, syrups, and similar indeterminate mixtures of carbohydrates met with in commercial analysis, instead of merely giving the polarizations, or the specific rotatory powers referred to the weights of the sample. The advantages are obvious. Such analytical results would be close approximations to the exact specific rotatory powers of the mixed anhydrous carbohydrates, and would be convenient of interpretation by inspection as being directly comparable on what is for all practical purposes an absolute standard and the one used in all strictly scientific work of the kind.

THE SPEED OF THE HYDROLYSIS OF STARCH BY ACIDS.[1]

The laws of the speed of hydrolysis of the carbohydrates with the exception of that of cane-sugar have been but little studied. Solomon[2] has collected some data on the action of various acids at boiling temperature. Welhelmy[3] showed in the case of the catalytic action of hydrochloric acid on cane-sugar that if the

1 We are greatly indebted to Prof. A. A. Noyes, of this department, for valuable aid in calculating the results of this work on speed of hydrolysis.

2 *J. prakt. Chem.*, (2), 28.

3 *Ber. d. chem. Ges.*, 18, 2211.

amount of acid and the temperature remained constant the rate of the inversion at any specified moment is proportional to the amount of unchanged sugar present at that moment.

That is, if A_0 represent the amount of sugar originally present, x the amount of this sugar changed over in any period of time, t, and c the reaction-constant, we have $\frac{dx}{dt} = c\ (A_0 - x)$.

The relative values of the constant, c, of the various acids in their action on cane-sugar have been determined by several observers, notably Ostwald,[1] who has compared, by means of their constants, the relative effect of chemically equivalent quantities of a large number of acids, taking the constant of hydrochloric acid as a standard with the arbitrary value of 100.

Recent work shows that acids act on salicin,[2] one of the glucosides, in a manner analogous to that of cane-sugar, the speed of hydrolysis of this body by the different acids bearing the same relation to hydrochloric acid.

The observations noted above suggested the possibility that in the hydrolysis of starch the acids would show the same proportional speed of reaction. This is an especially interesting problem because the starch molecule is exceedingly complicated, the molecular weight being undoubtedly very high. Starch hydrolysis, however, must be considered as somewhat different from that of cane-sugar or salicin. While these are easily soluble in cold water, starch is totally insoluble at ordinary room temperature. On the other hand, amylodextrin, the product of decomposition of starch by boiling water, is somewhat soluble in cold water, its solubility increasing with rise of temperature.

As by the customary procedure in determining speed of hydrolysis, it would be necessary to ascertain the exact moment when all the starch has been converted into the soluble form, a point not conveniently determined, we have adopted a method of measurement, based on the following principles:

The conversion products of starch, with the possible exception of those of very high rotatory power, are easily soluble in water, and can be looked upon as mixtures of maltose, dextrose and dextrin.

[1] *J. prakt. Chem.*, *1884*, 401.

[2] Noyes and Hall: *Ztschr. phys. Chem.*, *1895*, 240.

The starch first changes to amylodextrin. The hydrolysis then proceeds by successive stages through the so-called maltodextrin, maltose, and dextrose. "Reversion," so-called, may take place to some extent, a small amount of the dextrose forming dextrin-like bodies, "gallisin," "isomaltose," etc., but this point is not considered in this work. The dextrin may therefore be looked upon as the original substance hydrolyzed, and maltose and dextrose as successive products of the reaction.

Further, we have shown that whatever the condition of hydrolysis by acids, the specific rotatory power of any conversion product corresponds to a definite chemical composition, tables for determining which we have constructed.

Thus, for instance, a conversion product of 160° has been proved to contain 54.8 per cent. dextrin, the remainder being maltose and dextrose.

Hence, the time of taking any sample after the contents of the autoclave has acquired constant temperature, which requires about ten minutes, can be taken as the initial point for determining speed of hydrolysis, and all subsequent samples referred to this, as it is obvious that in any sample we can ascertain the dextrin unacted upon at that stage of the hydrolysis. The same holds true of maltose.

We have to deal with two reactions, the first being the hydrolysis of dextrin to maltose.

If A_0 is the amount of dextrin at the initial point taken, A_0-x, the amount remaining at any time, t, and c the constant depending on conditions of hydrolysis we get, $\frac{dx}{dt} = c\,(A_0 - x)$.

This, on integrating, gives $\log \frac{A_0}{A-x} = ct$, or $\frac{1}{t} \log \frac{A_0}{A_0-x} = c$, which is the general equation of a first-order reaction. The second decomposition is that in which maltose is hydrolyzed to dextrose, and is peculiar in so far as it proceeds simultaneously with that by which the maltose is formed. As a result of the hydrolysis of the dextrin the maltose increases rapidly to a maximum of 44.1 per cent. at a rotation of 129°.

It then gradually diminishes, while the dextrose percentage always increases.

Consequently, the equation expressing accurately the rate of change in the total amount of maltose present is quite complicated, and we have therefore used an approximate formula, which is sufficiently exact for the work in hand. The formula is derived from the exact differential equation

$$\frac{dD}{dt} = c_2 M,$$

which states that the amount of dextrose formed at each moment is proportional to the amount of maltose present by replacing the differential quantities by finite differences, which in applications of the formula must of course be taken small. In the place of M the average amount of maltose present during the interval of time considered is also substituted. That is, if M_1 and M_2 are the amounts of maltose present at the time, t_1 and t_2, and D_1 and D_2 the amounts of dextrose present at these same times, and c_2 is the reaction constant, we get as a result of the above mentioned substitutions:

$$D_2 - D_1 = c_2 \frac{M_1 + M_2}{2} (t_2 - t_1),$$

or,

$$\left(\frac{1}{t_2 - t_1}\right) \left(\frac{D_2 - D_1}{\frac{M_1 + M_2}{2}}\right) = c_2.$$

The results are contained in the following tables:

TABLE E.

SPEED OF HYDROLYSIS OF STARCH.

Time t. (minutes)	$[\alpha]^{20}_{D_{386}}$.	$A_0 - x$.	$\log \frac{A_0}{A_0 - x}$	C_1.	$\frac{D_2 - D_1}{\frac{m_1 + m_2}{2}}$	C_2.
Hydrochloric acid: 0.02 normal; at 2 A $T = 135°$ C.						
$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 161$; $A_0 = 55.8$.						
10	137	35.5	0.2216	0.02216	0.3581	0.0358
20	118	20.3	0.4391	0.02196	0.3118	0.0312
30	100	11.2	0.6784	0.02261	0.3790	0.0379
40	88	6.3	0.9684	0.02421	0.3274	0.0327
50	76	3.2	1.2415	0.02483	0.4638	0.0464
60	69	1.9	1.4678	0.02446	0.4162	0.0416
70	64	1.2	1.6674	0.02382	0.4264	0.0426
	$C_1 = 0.02344$.				$C_2 = 0.0373$.	

Sulphuric acid : 0.02 normal ; at 2 A $T = 135°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 177°$; $A_0 = 73.5$.

10	163	57.9	0.1036	0.01036	0.1954	0.0195
20	152	46.7	0.2248	0.01124	0.1436	0.0144
30	140	36.0	0.3100	0.01033	0.1703	0.0170
40	129	27.5	0.4270	0.01068	0.1678	0.0168
60	109	15.4	0.6788	0.01131	0.3656	0.0188
80	90	7.0	1.0212	0.01277	0.4700	0.0235
100	77	3.4	1.3348	0.01335	0.4809	0.0240
120	66	1.4	1.7202	0.01434	0.6915	0.0346

$C_1 = 0.0118$. $C_2 = 0.0211$.

Oxalic acid : 0.04 normal ; at 2 A $T = 135°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 180°$; $A_0 = 77.2$.

20	157	51.6	0.1750	0.00875	0.3147	0.0157
40	137	33.5	0.3626	0.00907	0.2890	0.0145
60	120	21.5	0.5552	0.00925	0.2738	0.0137
80	106	13.9	0.7446	0.00931	0.2762	0.0138
100	93	8.1	0.9791	0.00979	0.3224	0.0161
120	82	4.5	1.2344	0.00029	0.3426	0.0171
140	73	2.6	1.4726	0.01052	0.4149	0.0207

$C_1 = 0.00957$. $C_2 = 0.0159$.

Sulphurous acid : 0.02 normal ; at 2 A $T = 135°$ C.

$t_0 = 50$; $[\alpha]^{20}_{D_{386}} = 187°$; $A_0 = 87$.

50	179	76.0	0.0587	0.00117	0.1254	0.00251
100	172	67.7	0.1089	0.00109	0.0907	0.00181
150	165	60.0	0.1613	0.00108	0.1012	0.00202
200	159	53.7	0.2095	0.00105	0.0799	0.00159
250	151	45.7	0.2796	0.00112	0.1036	0.00207
300	144	39.3	0.3451	0.00115	0.0978	0.00196
350	137	33.5	0.4145	0.00119	0.1053	0.00211
400	131	29.0	0.4773	0.00119	0.0893	0.00179

$C_1 = 0.00113$. $C_2 = 0.00198$.

Acetic acid : 0.5 normal ; at 2 A $T = 135°$ C.

$t_0 = 50$; $[\alpha]^{20}_{D_{386}} = 170°$; $A_0 = 65.5$.

50	143	38.5	0.2307	0.00461	0.3775	0.00755
100	121	22.1	0.4718	0.00472	0.3516	0.00703
150	103	12.5	0.7193	0.00480	0.3643	0.00729
200	86	5.6	1.0680	0.00534	0.4638	0.00928
250	74	2.8	1.3690	0.00548	0.4969	0.00994

$C_1 = 0.00449$. $C_2 = 0.00822$.

Hydrochloric acid : 0.01 normal ; at 1 A $T = 121°$ C.

$t_0 = 40$; $[\alpha]^{20}_{D_{386}} = 183°$; $A_0 = 81.3$.

40	168	63.3	0.1087	0.00272	0.2118	0.00529
70	158	52.7	0.1883	0.00269	0.1358	0.00453
100	149	43.8	0.2686	0.00269	0.1199	0.00400
140	137	33.5	0.3851	0.00275	0.1764	0.00441
180	126	25.5	0.5036	0.00280	0.1693	0.00423
200	120	21.5	0.5777	0.00289	0.1028	0.00514
250	107	14.4	0.7517	0.00301	0.2539	0.00508

$C_1 = 0.00279$. $C_2 = 0.00467$.

Hydrochloric acid: 0.01 normal; at 2 A $T = 135°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 176°$; $A_0 = 72.3$.

10	162	56.9	0.1040	0.0104	0.1937	0.0194
20	148	42.9	0.2266	0.0113	0.1877	0.0188
40	128	26.8	0.4310	0.0108	0.3015	0.0151
60	110	16.0	0.6550	0.0109	0.3259	0.0163
80	93	8.1	0.9506	0.0119	0.4102	0.0205
100	81	4.3	1.2256	0.0123	0.3830	0.0182
120	70	2.0	1.5581	0.0130	0.4479	0.0294

$C_1 = 0.0115$. $C_2 = 0.0187$.

Hydrochloric acid: 0.01 normal; at 3 A $T = 145°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 174°$; $A_0 = 70$.

5	158	52.7	0.1233	0.0247	0.2766	0.0553
10	140	36.0	0.2888	0.0289	0.2528	0.0506
15	125	24.8	0.4506	0.0300	0.2351	0.0470
20	110	16.0	0.6410	0.0321	0.2756	0.0551
30	88	6.3	1.0458	0.0349	0.5544	0.0554
40	74	2.8	1.3979	0.0350	0.5630	0.0563
50	65	1.3	1.7212	0.0344	0.6349	0.0640

$C_1 = 0.0314$. $C_2 = 0.00548$.

Hydrochloric acid: 0.01 normal; at 4 A $T = 153°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 147°$; $A_0 = 42.0$.

5	117	19.7	0.3287	0.0657	0.4900	0.0980
10	96	9.4	0.6501	0.0650	0.4671	0.0934
15	79	3.8	1.0434	0.0696	0.5443	0.1088
20	68	1.8	1.3679	0.0684	0.6060	0.1212
25	61	0.85	1.6938	0.0678	0.7157	0.1431
30	57	0.5	1.9242	0.0641	0.7818	0.1564

$C_1 = 0.0668$. $C_2 = 0.1202$.

Hydrochloric acid: 0.04 normal; at 3 A $T = 145°$ C.

$t_0 = 5$; $[\alpha]^{20}_{D_{386}} = 150°$; $A_0 = 44.7$.

3	115	18.5	0.3831	0.1277	0.5736	0.1912
5	95	9.0	0.6961	0.1392	0.4541	0.2270
7	80	4.0	1.0481	0.1497	0.4833	0.2416
10	66	1.4	1.5042	0.1504	0.8083	0.2694
13	58	0.6	1.8721	0.1440	1.0350	0.3450
15	66	0.4	2.0482	0.1365	0.6285	0.3143

$C_1 = 0.1413$. $C_2 = 0.2648$.

Hydrochloric acid: 0.02 normal; at 3 A $T = 145°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 148°$; $A_0 = 42.9$.

5	116	19.1	0.3515	0.0703	0.5246	0.1029
10	96	9.4	0.6594	0.0659	0.4478	0.0896
15	80	4.0	1.0304	0.0687	0.5075	0.1015
20	69	1.9	1.3537	0.0677	0.5889	0.1178
25	61	0.85	1.7031	0.0681	0.7739	0.1548
30	56	0.45	1.9793	0.0660	1.0800	0.2160

$C_1 = 0.0678$. $C_2 = 0.1304$.

Hydrochloric acid : 0.01 normal ; at 3 A $T = 145°$ C.

$t_0 = 5$; $[\alpha]^{20}_{D_{386}} = 174°$; $A_0 = 70$.

5	158	52.7	0.1233	0.0247	0.2766	0.0553
10	140	36.0	0.2888	0.0289	0.2528	0.0506
15	125	24.8	0.4506	0.0300	0.2351	0.0470
20	110	16.0	0.6410	0.0321	0.2756	0.0551
30	88	6.3	1.0458	0.0349	0.5544	0.0554
40	74	2.8	1.3974	0.0350	0.5630	0.0563
50	65	1.3	1.7212	0.0344	0.6349	0.0640
	$C_1 = 0.0314$.				$C_2 = 0.0548$.	

Hydrochloric acid : 0.005 normal ; at 3 A $T = 145°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 172°$; $A_0 = 67.7$.

20	142	37.6	0.2554	0.0128	0.4270	0.0214
40	113	17.4	0.5901	0.0148	0.4900	0.0245
60	91	7.3	0.9673	0.0161	0.5226	0.0261
80	77	3.4	1.2991	0.0162	0.5082	0.0254
100	66	1.4	1.6845	0.0168	0.7429	0.0371
120	59	0.7	1.9855	0.0165	0.8172	0.0409
	$C_1 = 0.0155$.				$C_2 = 0.0279$.	

At the head of each table are given data as to the concentration and nature of the acid, the temperature corresponding to the steam pressure given in atmospheres and $[\alpha]^{20}_{D_{386}}$ at the initial time period t_0 with the corresponding value of A_0. Time values are expressed in minutes, and the constants c_1 for the hydrolysis of dextrin, c_2 for that of maltose, are calculated according to the formulas given above.

The results show that the constants in general are satisfactory, and that therefore the reaction like the sucrose inversion follows the law of the first order. It will also be seen that the values c_1 are much more uniform than those of c_2, which is to be expected since c_1 is absolute and c_2 only approximate. Deviations of c_1 may be fairly ascribed to variations in temperature which, though slight, are significant, owing to the high temperature coefficient of the reaction.

The dextrin values in Table C are consequently correct within the limits of error of analysis. It will be seen that the values of c_2 are much more constant in those determinations in which t is larger and the values of $[\alpha]_D$ decrease slowly. This was to be expected from the conditions of the approximate formula given above for the decomposition of maltose, these requiring that the amount of substance changed in a period of time must be small. The question of reversion may possibly have some

influence on the values of c_2 but as yet we are not prepared to express ourselves definitely on this subject.

The relative effects are shown in the following table: Table I shows the influence on the speed of hydrolysis of various acids at the same temperature, 135° C.

Table II shows the influence of temperature on the speed of hydrolysis when the same amount of acid is used.

Table III gives the influence of varying amounts of acid.

The mean value of constants are given in column II. Column III gives the relative value of the constants referred to that of $\frac{1}{100}N$ hydrochloric acid at 135° taken as 100. Column IV gives the velocity constants determined by Ostwald[1] for cane-sugar inversion by the same acids at half-normal concentration.

TABLE I.

Acid.	Concentration.	II.	III.	IV.
Hydrochloric	0.02 N	0.02344	100	100
Sulphuric	0.02 N	0.0118	50.35	53.6
Oxalic	0.04 N	0.00957	40.83	....
(")	(0.02 N)	(0.00479)	(20.42)	18.6
Sulphurous	0.02 N	0.00113	4.82	....
Acetic	0.5 N	0.00499	21.29	....
(")	(0.02 N)	0.00020	0.8	0.4

TABLE II.

Acid.	Concentration.	Temp.	I.	II.
Hydrochloric	0.01 N	121	0.00279	11.91
"	0.01 N	134	0.0115	49.07
"	0.01 N	145	0.0314	13.40
"	0.01 N	153	0.0668	28.50

TABLE III.

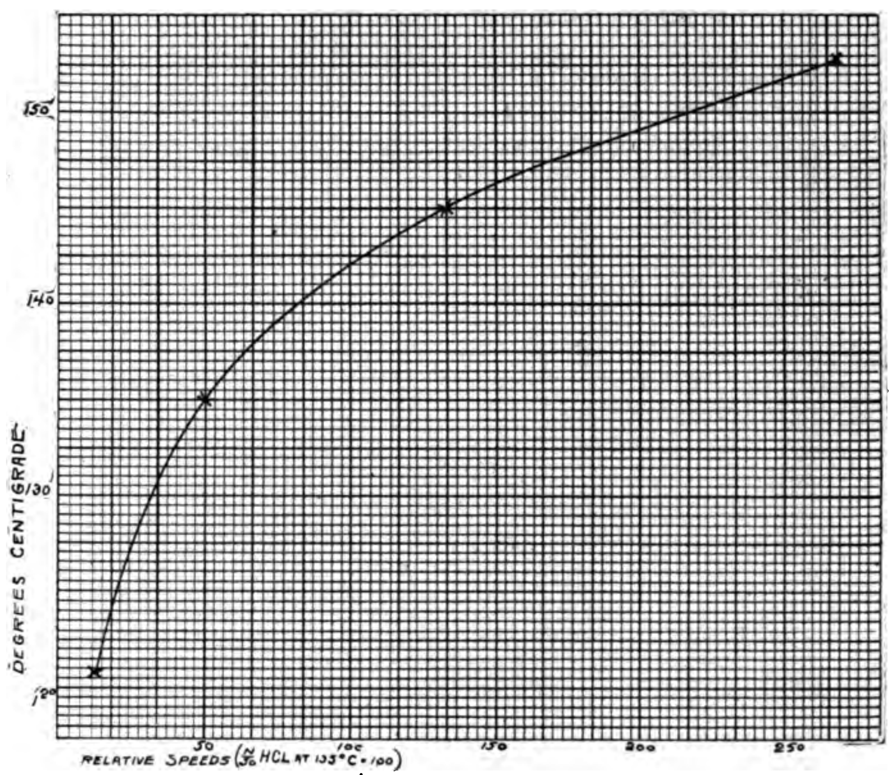
Acid.	Concentration.	II.	III.
Hydrochloric	0.04 N	0.1413	602.9
"	0.02 N	0.0678	289.3
"	0.01 N	0.0314	134.0
"	0.005 N	0.0155	66.13

It is seen that the corresponding numbers of columns III and IV agree fairly well. The relative influence of the various acids upon the hydrolysis of starch, sucrose and salicin are therefore nearly identical. It should be noted however that the chemical activity of hydrochloric acid on starch, as in the case of salicin

[1] *Loc. cit.*

and cane-sugar, increases in a greater ratio than the concentration, while the electrical conductivity increases more slowly.

The influence of temperature can be explained graphically by a curve approximating a parabola.



INFLUENCE OF TEMPERATURE

PLATE I.

Plate II shows the influence of the various acids.

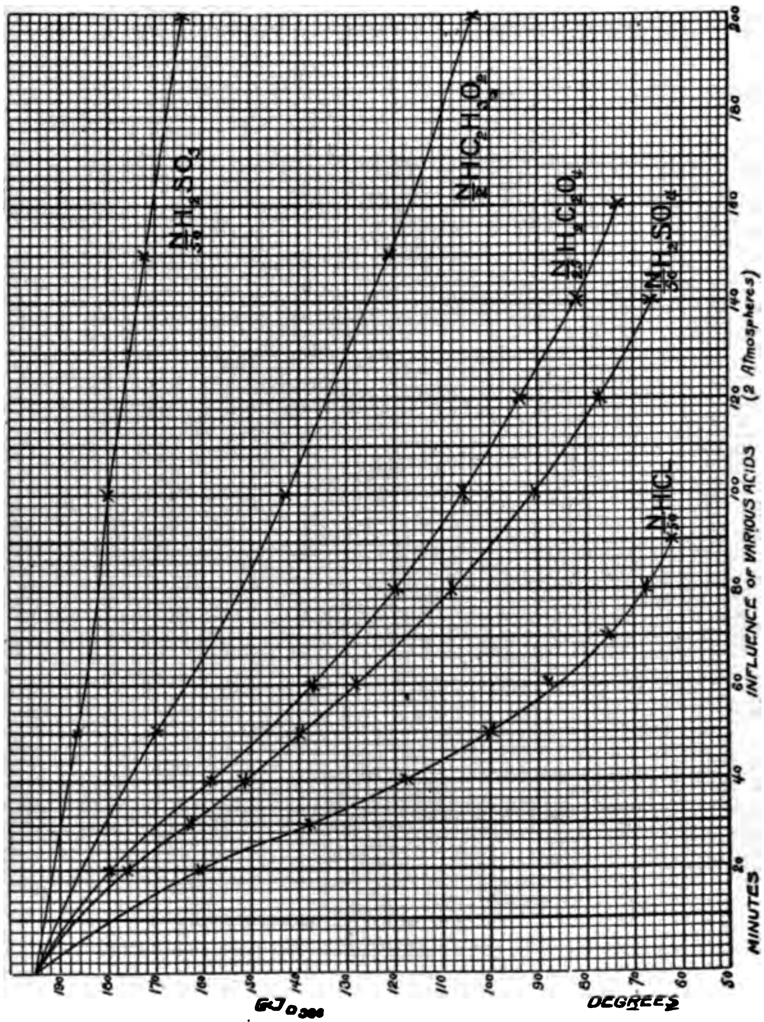


PLATE II.

Plate III shows the influence of the concentration, or amount of acid used.

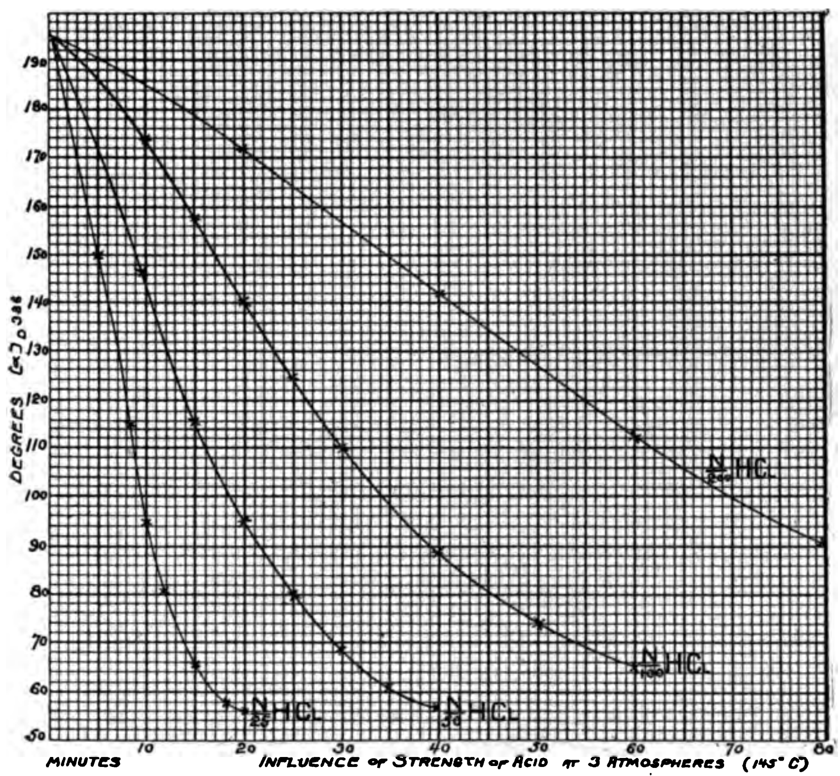


PLATE III.

Plate IV shows the relative curves due to temperature.

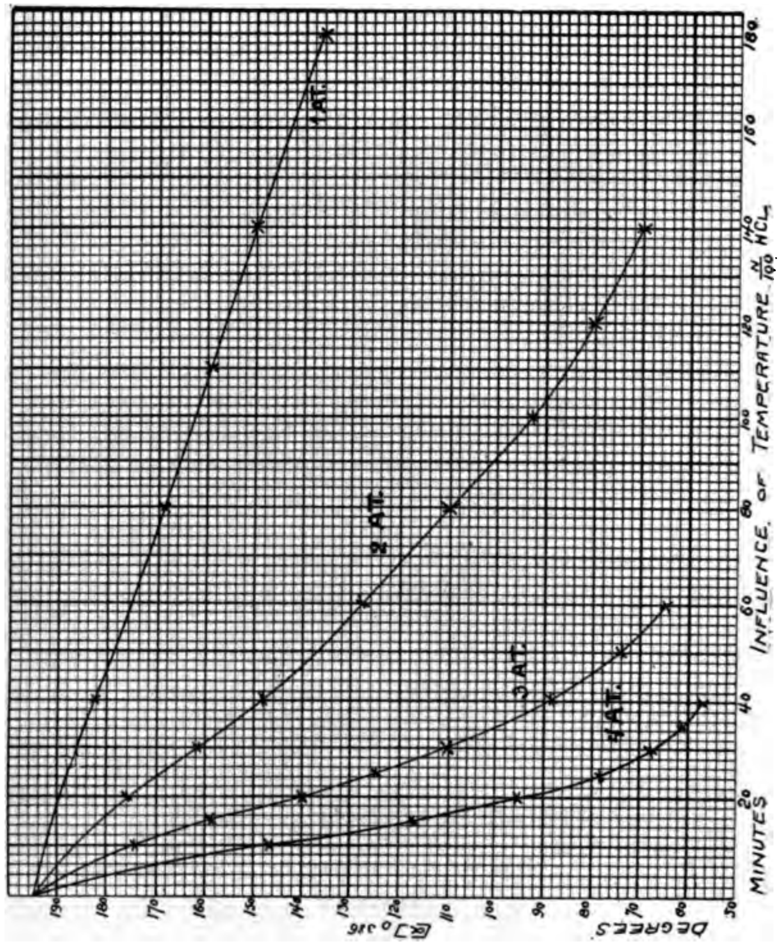


PLATE IV.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

NICKELO-NICKELIC HYDRATE, $Ni_3O_4.2H_2O$.

BY WILLIAM L. DUDLEY.

Received August 26, 1896.

IN studying the action of fused sodium dioxide on metals, I have obtained interesting crystalline compounds, some of which, at least, have never been described. Only one of them has been carefully investigated and it proves to be nickelo-nickelic hydrate, having the formula $Ni_3O_4.2H_2O$.

It is prepared by fusing sodium dioxide in a nickel crucible with metallic nickel at a cherry-red heat. The action of the oxide upon the nickel proceeds with moderate rapidity, and in a few minutes scaly crystals appear floating in the fused mass. The crystals multiply steadily until, in the course of an hour, the contents of the crucible is thick with them, and comparatively little liquid remains. After cooling, the crucible is submerged in a beaker of distilled water and the undecomposed sodium dioxide together with the sodium oxide dissolves out, leaving the crystals which rapidly settle to the bottom of the liquid. The crystals should be washed several times with boiling water by decantation, and finally thrown in a filter. It is quite difficult to wash out all of the alkali, which adheres with unusual persistence. Probably the best plan to adopt is to put the crystals in a Soxhlet extraction apparatus and wash with water until no coloration is obtained with phenolphthalein. This requires about fifty hours of continuous washing. The crystals should then be dried at 110° C. and a magnet passed carefully through them to remove any particles of metallic nickel which may have eroded and not been completely acted upon.

The crystals are lustrous and almost black, with a slight brown-bronze hue. They are soft, and grind in a mortar much like graphite. The crystals seem to be hexagonal plates, but measurements of the angles have not been made. They dissolve slowly in acids, forming nickelous salts. Hydrochloric acid evolves chlorine; sulphuric and nitric acids, oxygen. They are insoluble in water and in solutions of the alkalies. The compound is not magnetic. The specific gravity is 3.4115 at 32° C.

At 130° C. the compound does not undergo decomposition, but at about 140° C. it begins to lose weight; at 240° C. the weight

remains constant. At a red heat further loss is sustained and the residue remaining is nickelous oxide. The loss from 130° C. to 240° C. is due to water driven off, and at a red heat this loss is due to the evolution of oxygen.

The compound proved to be $Ni_3O_4.2H_2O$, as is shown by the results of the analysis:

Loss of H_2O on heating from 130° C. to 240° C.:

	Per cent.
First determination	13.00
Second "	13.13
Theory for $Ni_3O_4.2H_2O$	13.06

The residue remaining after heating to 240° C. is Ni_3O_4. On heating this residue to redness the loss of oxygen was found to be:

	Per cent.
Loss of oxygen	6.63
Theory	6.67

The total loss of water and oxygen obtained on heating the compound from 130° C. to redness was:

	Per cent.
First determination	18.91
Second "	18.88
Theory for $Ni_3O_4.2H_2O$	18.86

The oxygen given off on heating to redness was determined by calcining the compound in an atmosphere of carbon dioxide and collecting in Schiff's apparatus over potassium hydroxide solution. The result gave:

	Per cent.
Oxygen	5.93
Theory for $Ni_3O_4.2H_2O$	5.84

The nickel was determined and found to be:

	Per cent.
Nickel	63.67
Theory	63.72

In all of the calculations the atomic weight of nickel was taken to be 58.56 and oxygen 16.

The compound made in a nickel crucible of commerce is not perfectly pure, as the sample obtained was found to contain 0.71 per cent. of cobalt, the presence of which, however, would make no appreciable difference in the results of the analyses. No method has been found for freeing the compound from this im-

purity, and it appears at present as if the only plan would be to use a chemically pure nickel crucible in making it, for no crucible will withstand the action of fused sodium dioxide. Porcelain, iron, silver, gold and platinum crucibles are rapidly attacked.

The presence of water in this compound seems curious, but it may be due to the presence of sodium hydroxide in the sodium dioxide. Again it may be due to the water added to dissolve the soluble residue from the crystals. The first explanation seems to be the more plausible since the crystals are formed in the mass while it is fused, and they are not produced upon the addition of the water. If such is the case it would seem that the water driven off between 130° C. and 240° C. is from the breaking down of a true hydrate, rather than the expulsion of water of crystallization.

A cobalto-cobaltic hydrate, $Co_3O_4.2H_2O$, has been described,[1] but it was obtained by exposing to moist air, Co_3O_4, prepared by heating cobalt carbonate. Ni_3O_4, prepared by heating nickelo-nickelic hydrate to 240° C. is hygroscopic and absorbs about seven and four-tenths per cent. of water from the air at 30° C., which is completely lost at 110° C., showing that no hydrate is formed under these conditions.

The study of the action of fused sodium dioxide on the metals will be continued here, and it is hoped that some more data can be contributed soon.

VANDERBILT UNIVERSITY.

TABLE OF FACTORS.

BY EDMUND H. MILLER AND J. A. MATHEWS.

Received August 6, 1896.

ATOMIC masses, based on O = 16, taken from an article by F. W. Clarke, this Journal, March, 1896.

	Required.	Factor.	Logarithm.
$AlPO_4$	Al.	0.221976	$\bar{1}.3463071$
	Al_2O_3.	0.418489	$\bar{1}.6216835$
Sb_2O_4	Sb.	0.790067	$\bar{1}.8976643$
Sb_2S_3	Sb.	0.714570	$\bar{1}.8540446$
As_2S_3	As.	0.609522	$\bar{1}.7849890$
$Mg_2As_2O_7$	As.	0.483268	$\bar{1}.6841870$
Ag_3AsO_4	As.	0.162234	$\bar{1}.2101418$
$BaSO_4$	BaO.	0.657088	$\bar{1}.8176234$

[1] Genth and Gibbs: *Am. J. Sci.*, 23, 257.

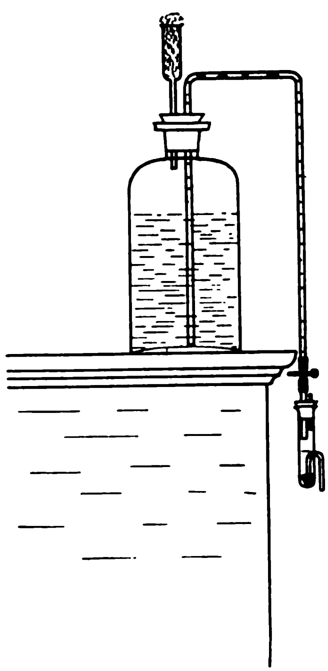
	Required.	Factor.	Logarithm.
	SO_3.	0.342912	$\bar{1}.5351829$
	S.	0.137342	$\bar{1}.1378121$
Bi_2O_3	Bi.	0.896600	$\bar{1}.9525990$
$CaCO_3$	CaO.	0.560296	$\bar{1}.7484173$
$CaSO_4$	CaO.	0.411899	$\bar{1}.6147904$
	$CaCO_3$.	0.735145	$\bar{1}.8663731$
CO_2	C.	0.272893	$\bar{1}.4359916$
Cr_2O_3	Cr.	0.684791	$\bar{1}.8355581$
$3K_2SO_4.2CoSO_4$	Co.	0.141511	$\bar{1}.1507892$
CuO	Cu.	0.798995	$\bar{1}.9025440$
Cu_2S	Cu.	0.798644	$\bar{1}.9023531$
Fe_2O_3	Fe.	0.700076	$\bar{1}.8451446$
Fe	Fe_2O_3.	1.42842	0.1548554
	FeO.	1.28561	0.1091100
	Fe_3O_4.	1.38082	0.1401359
$PbCrO_4$	Pb.	.640500	$\bar{1}.8065193$
$PbSO_4$	Pb.	.682927	$\bar{1}.8343742$
$Mg_2P_2O_7$	P.	.278681	$\bar{1}.4451076$
	P_2O_5.	.638038	$\bar{1}.8048465$
	MgO.	.361962	$\bar{1}.5586631$
	$MgCO_3$.	.757343	$\bar{1}.8792934$
Mn_3O_4	Mn.	.720490	$\bar{1}.8576283$
$Mn_2P_2O_7$	Mn.	.387226	$\bar{1}.5879648$
$(NH_4)_2PtCl_6$	Pt.	.439205	$\bar{1}.6426669$
	N.	.063281	$\bar{2}.8012744$
	NH_3.	.076911	$\bar{2}.8859881$
	NH_4Cl.	.241235	$\bar{1}.3824396$
Pt from $(NH_4)_2PtCl_6$	N.	.144081	$\bar{1}.1586075$
	NH_3.	.175114	$\bar{1}.2433212$
	NH_4Cl.	.549253	$\bar{1}.7397727$
K_2PtCl_6	KCl.	.306951	$\bar{1}.4870695$
	K_2O.	.193944	$\bar{1}.2876767$
KCl	K_2O.	.631840	$\bar{1}.8006072$
K_2SO_4	K_2O.	.540593	$\bar{1}.7328706$
SiO_2	Si.	.470199	$\bar{1}.6722814$
AgBr	Br.	.425560	$\bar{1}.6289611$
AgI	I.	.540313	$\bar{1}.7326479$
AgCl	Cl.	.247262	$\bar{1}.3931579$
	Ag.	.752738	$\bar{1}.8766436$
NaCl	Na_2O.	.530769	$\bar{1}.7249057$
Na_2SO_4	Na_2O.	.436801	$\bar{1}.6402836$
SnO_2	Sn.	.788150	$\bar{1}.8966087$
TiO_2	Ti.	.600749	$\bar{1}.7786928$
ZnO	Zn.	.803464	$\bar{1}.9049663$
$Zn_2P_2O_7$	Zn.	.429115	$\bar{1}.6325737$
$ZnNH_4PO_4$	Zn.	.366438	$\bar{1}.5640011$

RAPID MEASURING PIPETTE.

By Edward L. Smith.

Received August 4, 1896.

THE apparatus described below is a device for rapidly measuring and discharging a definite volume of liquid. It may be well to state at this point that the principle is not applicable in all, or in even the majority of cases, where it is desired to measure and discharge liquid reagents in the laboratory. Where extreme accuracy is essential, the ordinary pipette or a burette must still be used. Perhaps the best way to explain the utility of the apparatus will be to state the exact use to which it is put in our laboratory. In the course of some experiments with sand filters, samples of the different effluents as well as of the applied sewage were taken daily, treated with a small quantity of a concentrated sterilizing agent, and an analysis made each week of the combined daily samples.



It was to measure and discharge this sterilizing solution that the apparatus was devised. The quantity added in each case was five cc. Of course a variation from that amount of one- or two-tenths cc. would not materially affect the results and the great advantage in convenience and rapidity over the use of the common pipette for the same purpose is admitted by all who have seen the apparatus work. A large bottle forms the reservoir. The stopper of this bottle carries two tubes. One simply serves to admit air and contains a loose plug of cotton to exclude dust, etc. The other tube is bent to form an ordinary siphon and the end of the longer limb is attached to a short glass tube by means of a rubber connection,

provided with a pinch-cock. The short glass tube to which reference was just made passes through a stopper inserted into the mouth of an ordinary test-tube. Through a hole blown in the side of this tube another glass tube, bent to form a siphon, is inserted and fastened in place by a piece of rubber tubing of the proper size, slipped on over the tube. The leg of the siphon inside the test-tube is of such a length that when the pinch-cock above is opened and the liquid allowed to enter the test-tube, five cc. will be automatically discharged when the level of the liquid has reached a mark on a line with the top of the bend in the siphon tube.

The apparatus can be constructed in a few moments in any laboratory, and for purposes to which it is adapted, it will, I am sure, be found satisfactory. It may be asked, what is the advantage of the form suggested over the ordinary burette with supply tubes? The answer is, it does away with the necessarily oft-repeated filling of the burette, and there is but one mark to watch in making the measurement—that previously mentioned, on the test-tube. The tubing used is of such size that a rapid discharge is insured, the time required being less than would be the case were a burette employed.

MERCURIC CHLOROTHIOCYANATE.

By Charles H. Herty and J. G. Smith.

Received August 8, 1896.

It has been shown by one of us[1] that the so-called compound lead iodochloride, PbICl, is not a true chemical compound, but a mixture of lead iodide and lead chloride.

It has seemed advisable, therefore, to study more fully the nature of the compound mercuric chlorothiocyanate, HgCl(CNS), described by McMurtry.[2] To this end a series of solutions was prepared, in one of which was used the exact proportions of mercuric thiocyanate and mercuric chloride given by McMurtry for the preparation of mercuric chlorothiocyanate; in the other members of the series, arbitrarily taken quantities of the one salt were replaced by equivalent quantities of the other. The

[1] *Am. Chem. J.*, 18, 290.
[2] *J. chem. Soc.*, *1889*, 50.

mixed salts were completely dissolved in hot water and the solutions allowed to cool and crystallize. The quantities actually used were :

Name.	Mercuric thiocyanate. Grams.	Mercuric chloride. Grams.	Water. cc.
A	9.5000	3.1439	2000
B	6.7500	65.5004	750
C	5.5000	6.5715	550
D (McMurtry)	5.0000	7.0000	450
E	4.5000	7.4285	350
F	3.5000	8.2853	300
G	1.0000	10.4296	200

On cooling, crystals separated from all of the solutions except *G*. The crystals from *A*, *B*, *C*, and *D* were fern-shaped, while those from *E* and *F* were prismatic.

By evaporating the solution *G* one-half, quite a good crop of prismatic crystals was obtained. The crystals from all of the solutions were separated from the mother-liquor by filtration and rapid pressing between folds of drying paper.

From the mother-liquor of *D* two crops of prismatic crystals were obtained by evaporating to one-half and then to three-fourths of original volume. These were designated D' and D''.

The character of the various crops of crystals was determined by estimating the mercury present in each. This was done by reducing the compounds with sodium peroxide, as recommended by Schuyten,[1] and weighing the mercury. Analysis showed :

		Mercury calculated for		
	Mercury found, per cent.	Mercuric thiocyanate, per cent.	Mercuric chlorothiocyanate, per cent.	Mercuric chloride, per cent.
A	62.72	63.28	68.12	73.85
B	62.76	....	....	....
C	62.74	....	....	....
D	63.91	....	....	....
E	68.24	....	....	....
F	68.67	....	....	....
G	72.59	....	....	....
D'	....	68.45	....	....
D''	....	....	72.41	....

These results show that the various crops of crystals fall into three classes, mercuric thiocyanate, mercuric chlorothiocyanate, and mercuric chloride. This was confirmed by inspection with

[1] *Chem. Ztg.*, 20, 239.

the microscope. Further, the three successive crops of crystals from solution *D* are seen to be the first mercuric thiocyanate, slightly contaminated by mercuric thiocyanate, as proved both by the high analytical result and by microscopic inspection, the second crop is mercuric chlorothiocyanate, and the third mercuric chloride.

The low results in the case of the pure salts is undoubtedly due to the fact that the filters containing the reduced mercury were dried at the ordinary temperature with consequent slight volatilization of mercury.

The effect of crystallization upon the salt mercuric chlorothiocyanate was next tried. A portion of the salt was dissolved in hot water just sufficient for complete solution. On cooling crystals separated, which, under the microscope, were seen to be only mercuric thiocyanate. The mother-liquor from these, on evaporating one-half, yielded only mercuric chlorothiocyanate. On evaporating the mother-liquor from this last two-thirds the crystals formed are seen to be a mixture of crystals of mercuric chlorothiocyanate and mercuric chloride. Finally, on evaporating this mother-liquor to dryness spontaneously, only crystals of mercuric chloride were obtained. The substance therefore undergoes dissociation when dissolved in water.

From all of the above it would seem that mercuric chlorothiocyanate is a true chemical compound, and further, that the only compound which can be prepared from solutions of mercuric chloride and mercuric thiocyanate is that represented by the formula $Hg<^{Cl}_{CNS}$ or $HgCl_2.Hg(CNS)_2$.

These results varying so widely from those obtained in the case of lead iodochloride suggest the question: is the difference due to the fact that in the one case we have the more closely related groups, iodine and chlorine, while in the other we have the more different groups, thiocyanogen and chlorine, or is the difference due to the fact that in the one case we have a lead compound while in the other a mercury salt? To test this point work will be begun at once on mixtures of lead chloride and lead thiocyanate.

UNIVERSITY OF GEORGIA.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

XXIV.—COMPOSITION OF AMERICAN KAOLINS.

BY CHARLES F. MABERY AND OTIS T. KLOOZ.[1]

Received July 22, 1896.

ALTHOUGH great advances have been made in recent years toward a better knowledge of American clays and suitable methods for the manufacture of ware from them, much more extended investigation is necessary, both concerning the composition of the great clay deposits and in the details of manufacture. The first and most essential information is a correct knowledge of the composition of all clays available for use. Of scarcely less importance is masterly skill in the purification of crude materials, shaping the ware and burning. In the preparation of materia lsit is questionable whether American manufacturers can wait patiently several months for the slow processes of lixiviations and kneading that European porcelain makers have found indispensable in the production of the finest porcelain. The great porcelain factories in Europe are founded on the application of scientific skill and a personality in shaping and burning, handed down by lineal descent through many generations. Is it possible to procure for American factories scions for those ancient families, or must we wait for its perfection by our own ready facility and ingenuity?

As already mentioned, the porcelain manufacturer must be perfectly familiar with the composition of all materials within his reach. In making suitable mixtures he must have before him as one of the most essential features of composition, the proportions of free and combined silica, as well as the percentages of lime, iron, alkalies and water.

Having at hand a collection of clays, including representatives of American deposits, as well as several specimens from famous factories in Germany, it seemed of interest to compare the composition of clays from different sources. For the manufacture of the finest porcelain, the kaolin used in the Royal Berlin factory, at Charlottenburg, may be accepted as a standard of comparison. As every one knows who is familiar with the

[1] This work was offered by Mr. Klooz in a thesis for the degree of Bachelor of Science.

qualities of true porcelain, the products from this factory are approached by no other in the world. The composition of the kaolin used in the manufacture of this ware is shown by the following analysis of the clay, two specimens selected at different times, from great quantities within the Berlin factory.

	I.	II.
Combined water	6.00	7.65
Silica	72.16	65.70
Alumina	20.05	24.49
Iron	0.10	1.03
Lime	1.14	0.60
Magnesia	0.02	0.26
Sodium oxide	0.12	0.23
Potassium oxide	0.41	0.03
Free silica	49.84	44.93

The different percentages in these analyses indicate that some latitude is permissible, although a high percentage of silica is evidently essential. These analyses show nearly the same composition as is given in the numerous analyses of the most celebrated clays of the German factories, especially in the low percentages of lime, iron and alkalies, and the large proportion of silica. An analysis of biscuit ware from the same factory shows nearly the same composition. Apparently the clay has the required proportion of silica without further addition:

Silica	68.24
Alumina	29.16
Iron	0.10
Lime	1.18
Magnesia	0.12
Alkalies	0.17
Free silica	57.50

Of the American clays, analyses showed that some contained a considerable excess of silica above the amount required for the oxygen ratio of silica to that of the alumina, 2 : 1, or the formula $Al_2O_3.3SiO_2$, which is accepted in the manufacture of the best German ware; others only a small excess of silica. Of the high silica clays, a specimen from a deposit in Maryland gave the following results:

Combined water	11.23
Silica	47.60
Alumina	37.38
Iron	1.66
Lime	1.50
Sodium oxide	0.22
Potassium oxide	0.34
Free silica	17.10

Another clay of this class is a Missouri kaolin which was analyzed:

Combined water	4.15
Silica	82.64
Iron	12.41
Lime	0.05
Magnesia	0.11
Sodium oxide	0.08
Potassium oxide	0.53
Free silica	69.45

The following analysis represents another high silica clay from Black Rock, Arkansas:

Combined water	3.98
Silica	84.24
Alumina	11.50
Iron	0.08
Lime	0.52
Magnesia	0.02
Sodium oxide	trace
Potassium oxide	0.42
Free silica	69.93

Another high silica clay is from Milton Hollow, Middlesex Co., N. J.:

Combined water	5.52
Silica	75.06
Alumina	18.32
Iron	0.08
Lime	0.80
Magnesia	0.14
Potassium oxide	0.25
Free silica	59.71

A specimen of clay from a deposit in Washington, Middlesex Co., N. J., also showed a high percentage of silica:

Combined water	2.00
Silica	89.16
Alumina	5.77
Iron	0.07
Lime	0.70
Magnesia	0.12
Potassium oxide	1.29
Sodium oxide	1.31
Free silica	80.30

A clay having nearly the same composition as the specimen from the Berlin factory, is from a deposit at Hockessen, Delaware :

Combined water	6.55
Silica	71.46
Alumina	21.02
Iron	0.08
Lime	0.54
Magnesia	0.14
Potassium oxide	0.33
Sodium oxide	0.36
Free silica	53.13

It should not be inferred from the foregoing analyses that all American clays are high in silica. Some of the largest and most important deposits contain very little free silica. One of the purest kaolins is found in large quantities in Indiana, and the following analysis shows its composition :

Combined water	15.09
Silica	44.23
Alumina	40.56
Iron	0.07
Lime	0.13
Magnesia	0.10
Potassium oxide	0.10
Sodium oxide	0.15
Free silica	2.41

A clay of somewhat similar quality is found in Northampton Co., Pa. :

Combined water	11.20
Silica	48.16
Alumina	37.24
Lime	2.00
Magnesia	0.29
Iron	1.16
Potassium oxide	0.25
Sodium oxide	0.08
Free silica	2.85

A paper clay from South Amboy, N. J., Middlesex Co., gave the following results on analysis:

Combined water	13.35
Silica	43.30
Alumina	42.45
Iron	0.09
Lime	0.34
Magnesia	0.10
Potassium oxide	0.44
Sodium oxide	0.08
Free silica	3.55

A washed clay used in the manufacture of china, from New Castle, Del., gave the following composition:

Combined water	12.95
Silica	47.42
Alumina	38.42
Iron	0.08
Lime	0.70
Magnesia	0.12
Potassium oxide	0.30
Sodium oxide	0.12
Free silica	4.79

A clay in Woodbridge, Middlesex Co., N. J., also used in the manufacture of ware, is nearly pure kaolin:

Combined water	14.34
Silica	44.34
Alumina	38.09
Iron	0.15
Lime	0.96
Magnesia	0.10
Potassium oxide	1.00
Sodium oxide	0.79
Free silica	1.33

It is interesting to compare the composition of American kaolins with a standard kaolin used in England:

Combined water	13.00
Silica	46.00
Alumina	40.00
Iron	0.33
Lime	0.33
Magnesia	0.33

Several of the clays analyzed are used in the manufacture of ware. From some of these deposits specimens have been analyzed, and the results given in the "Chemistry of Pottery," by K. Langenbeck, are not essentially different from those given in this paper.

It is evident that the wide differences in the proportions of clay and silica in American kaolins render it imperatively necessary that they be taken into account in the selection of materials for the manufacture of ware. It is also evident that the United States is not wanting in an abundance of material for the manufacture of ware equal to the best foreign production.

DISCUSSION.

Wm. McMurtrie: It is an interesting fact not brought out here, that in many of the clays of New Jersey, and I think particularly from some of the deposits represented in the tables, Prof. Geo. H. Cook reported appreciable quantities of titanic oxide amounting to one-half per cent. more or less. The same constituent has been found in clays from other localities which I do not now exactly remember, but I have been led to believe that the existence of titanic oxide may be expected in a good many American clays.

W. A. Noyes: I have analyzed a number of Indiana clays and have found titanic oxide with but one exception. The Indiana clay given corresponds closely with one I analyzed last fall, and that particular one is free from titanic oxide, or practically so. All the other clays, and I feel safe to say that all these clays must contain titanic oxide.

The President: Does anyone know the effect of titanium on the ware?

A. A. Breneman : My impression is that Seger says there seems to be a connection between the peculiar light gray of salt-glazed stoneware, a color which is unique, and the presence of titanium. That is a very interesting statement, because that peculiar form of whitish or bluish gray stoneware is very characteristic, and I see nothing in the presence of iron alone in the clay sufficiently to account for it.[1]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

XXV. COMPOSITION OF CERTAIN MINERAL WATERS IN NORTHWESTERN PENNSYLVANIA.[2]

BY A. E. ROBINSON AND CHARLES F. MABERY.

Received July 26, 1896.

THE therapeutic qualities of mineral springs throughout northwestern Pennsylvania have long been recognized, and recently some of these springs, notably those at Saegertown and Cambridgeboro, have come into prominence through the enterprise of persons interested in hotels and sanitariums. The desirable qualities of these waters are doubtless dependent on

[1] NOTE ON TITANIUM IN CLAYS.—In the course of a discussion of Prof. Mabery's paper on American clays at the Buffalo meeting I alluded to the peculiar color of salt-glazed stoneware, and ascribed to Seger the suggestion that it was due to the presence of titanium. On referring to Seger's article (Wagner's Jahresbericht, 1883, p. 625), I find that he says that titanic acid (13.3 per cent.) heated with a very pure kaolin to a temperature between the melting points of wrought iron and platinum fuses, and that titanic acid is, under similar conditions, more of a flux for clay than silicic acid is. In the proportion of 6.65 per cent. of TiO_2, the mass became only semi-fused, and exhibited a dark-blue gray color. He says this color suggests the tint given by many clays when strongly heated.

Morgenroth (Wag. Jahr., 1884, 638) says, however, that rutile gives to clay ware a gray color under the glaze when impure ferruginous clays are used, but a yellow, ivory-like tint with pure clays. As rutile was used in the proportion of only 0.4 per cent., the minute proportion of iron which it carries (1.5 to 2.4 per cent. Fe_2O_3) would have little effect.

The interpretation of these facts to explain the peculiar gray color of salt-glazed stoneware, was probably a suggestion of my own, made at the time of reading these articles a dozen years ago. It was ascribed in the course of the discussion to Seger, as my "impression."

Nevertheless, in view of the peculiarity of this color, the gray of salt-glazed ware which is uniform throughout the body and becomes more bluish in overburned pieces, and in view also of the presence of iron in the rather crude clays used for the ware, and the fact that iron alone tends to escape as volatile chloride in presence of the salt used for glazing, the suggestion is worthy of note. A. A. BRENEMAN.

[2] This work, with a study of the methods of analysis, was offered by Mr. Robinson in a thesis for the degree of Bachelor of Science. Read at the Buffalo Meeting, August, 1896.

iron and certain other salts, especially on the bromides, and it is a popular view that lithium salts sometimes present impart valuable medicinal qualities. A quantity of water was collected from one of these surface springs at Conneautville by one of us (Robinson) and its composition as shown by analysis may serve as a representative of the springs in this region. The total solids in this water is equivalent to 6.586 grains per imperial gallon, or 9.83 parts per 100,000. Evidently the combination of bases and acids is to a certain extent arbitrary, but this distribution accounts for the total quantities of the various elements given by analysis :

	Grains per gallon.
Potassium carbonate	0.985
Lithium carbonate	0.002
Sodium chloride	0.925
Calcium bicarbonate	2.879
Calcium sulphate	1.291
Magnesium chloride	0.204
Ferrous carbonate	0.743
Silica	0.233
Hydrogen sulphide	trace

The specific gravity of this water was found to be 1.0002 at 20°. Evidently the analysis shows the composition of a good potable water. Any medicinal qualities it possesses must be referred to the iron and perhaps to a less extent to the lithium.

At greater depths in this section of Pennsylvania and in certain portions of Ohio, water may be found that partakes in a greater degree of the qualities imparted by the constituents of bittern. Wells sunk to depths of 1,000 to 3,000 feet have penetrated strata enclosing, frequently under great pressure, large quantities of bittern waters. While in general conforming in composition to the salts contained in bittern, occasionally these wells have yielded peculiar results on analysis. Such an aqueous stratum was reached several years ago at Conneautville, Crawford County, Pa., in an endeavor to obtain oil or gas. The drill penetrated the formation enclosing water at a depth of 2,667 feet and the drilling tools were forced upwards to a height of 1,800 feet by the water which prevented further drilling. This

level was maintained notwithstanding vigorous attempts to clear the well by pumping. A slight examination then showed that this water possessed peculiar qualities, but the well received no further attention until within a few months ago when it was cleared and a quantity of the water was procured for a more thorough examination. The total solids is equivalent to 21,334.34 grains per gallon or to 30,536 parts per 100,000. The specific gravity of the water is 1.205 at 15°. Its composition as shown by the results of analyses is as follows:

	Grains per gallon.	Parts per 100.000.
Potassium chloride	528.577	755.6
Lithium "	56.422	80.3
Ammonium "	151.879	216.6
Sodium "	9902.578	14430.0
Potassium bromide	137.010	245.7
" iodide	2.078	2.96
Magnesium chloride	2172.499	3096.0
Calcium "	8335.537	11880.0
" sulphate	7.886	11.1
Ferrous carbonate	114.836	163.5
Aluminum chloride	21.816	31.1
Silica	3.220	4.6
Hydrogen sulphide	0.033	0.05

There are certain features of this water that deserve especial mention. The large proportion of ammonium chloride is quite unusual in waters from such depths. Lithium chloride is frequently found in surface springs, and in brines from deep wells, but rarely, if ever, in such quantities as this water contains. If lithium salts impart to spring water the therapeutic qualities claimed for them, it is not difficult to account for the beneficial effects that have been observed in the use of this water. No doubt the large proportion of potassium bromide has much to do with the marked sedative effect. The large percentage of potassium iodide is also phenomenal, and it must intensify the mineral characteristics of the water. Besides the characteristics of a bromo-lithia water the large percentage of iron assures the desirable qualities of an iron water. The peculiar composition of this water, especially in the large quantities of the rarer elements, offered a favorable opportunity to ascertain whether these

bittern deposits contain also the elements, cesium and rubidium, which are rarely found in springs. Forty-five liters of the water were evaporated to a small volume, removing the great quantities of salt as they separated. When the volume was reduced to less than fifty cc. this solution as well as the lixiviated salts that had separated during evaporation were carefully examined in the spectroscope. But not a trace of rubidium nor cesium could be detected. It is therefore safe to conclude that the bittern deposits from the ancient sea do not contain these rarer elements.

It may not be out of place to remark that the chemical composition of this water explains the remarkable therapeutic qualities especially for rheumatism and nervous diseases that it has been found to possess.

SOME ANALYTICAL METHODS INVOLVING THE USE OF HYDROGEN DIOXIDE.[1]

By B. B. Ross.

Received August 31, 1896.

THE use of hydrogen peroxide as a laboratory reagent, although originally restricted to a few operations of minor importance, has within recent years met with a much wider extension, and its numerous applications in both qualitative and quantitative analysis, render it at present almost indispensable in every well-equipped analytical laboratory.

Among the more interesting applications of this substance in quantitative estimations are those which are based on the reaction which takes place when an excess of hydrogen dioxide is brought in contact with an acid solution of chromic acid, and Baumann[2] several years since described quite fully a number of analytical processes growing out of the reaction referred to.

In the process for the estimation of chromic acid in soluble chromates as outlined by Baumann, the substance under examination is first brought into a state of solution, and the not too concentrated liquid is transferred to a generating flask of special construction.

[1]Read at the Buffalo meeting, August 22, 1896.

[2] *Ztschr. anal. Chem.*, 31, 436.

Ten cc. of dilute sulphuric acid are next added, after which from five to ten cc. of commercial hydrogen peroxide are run in from a small closed vessel connected with the generating flask, while the oxygen which is evolved, after the vigorous shaking of the contents of the flask, is collected over water in an azotometer.

The following equations given by Baumann illustrate the chemical changes connected with the above described reaction:

$$K_2Cr_2O_7 + H_2O_2 + H_2SO_4 = K_2SO_4 + 2H_2O + Cr_2O_7;$$
$$Cr_2O_7 + 3H_2SO_4 + 4H_2O_2 = Cr_2(SO_4)_3 + 7H_2O + O_8.$$

From these equations it will be seen that for two molecules of chromic acid or one molecule of potassium dichromate, there are evolved eight atoms of oxygen, giving an equivalent of 445.3 cc. of oxygen (measured at 0° C. and 760 mm. pressure) for each gram of chromic acid which may be present.

The writer, soon after the appearance of the original article by Baumann, made a number of experimental tests of this method with a view to applying it to some other analytical processes, and still more recently has conducted a series of tests for the purpose of determining the adaptability of Baumann's method to the indirect volumetric estimation of iron.

In the dichromate method for the volumetric determination of iron, as commonly employed, the end point of the oxidation process is ascertained by the reaction with potassium ferricyanide.

As the end of this reaction is almost invariably difficult to determine, particularly if zinc has been employed as a reducing agent, the dichromate process has met with but limited application.

In order to apply the principle of the chromic acid method of Baumann to the estimation of iron, an excess of dichromate solution was employed in all of the tests and experimental determinations, the amount of the excess of chromic acid being determined by the volume of oxygen evolved upon treatment with hydrogen dioxide.

The mode of procedure adopted was as follows:

A dichromate solution was prepared by dissolving 4.913 grams

of C. P. crystallized potassium dichromate in water and diluting to a bulk of one liter.

The iron solution employed in standardizing the dichromate and permanganate solutions was obtained by dissolving iron wire in dilute sulphuric acid, the solution being reduced with metallic zinc, as usual, previous to titration.

The dichromate solution was also titrated against a freshly prepared solution of ammonium ferrous sulphate, the strength of which had been determined by titration with permanganate solution, which had also been carefully standardized by means of iron wire.

In order to ascertain the strength of the dichromate solution by the hydrogen dioxide method, about fifteen cc. of the dichromate solution is run into the generating flask above referred to, and there is also added an amount of ferric sulphate solution (free from ferrous sulphate) equivalent to about 0.06 to 0.10 gram of iron. The object of employing the ferric sulphate in this standardization is to supply approximately the same conditions as obtain in the process for the actual determination of iron.

The amount of oxygen given off from chromic acid in the presence of ferric sulphate is slightly less than that evolved when ferric sulphate is absent, but the amount of ferric iron present may vary considerably without affecting the volume of oxygen liberated.

To the contents of the generating vessel about ten cc. of dilute sulphuric acid are now added, and the flask is then connected by means of a rubber tube with a Schulze's azotometer, which has been filled with water to the zero point.

From five to ten cc. of hydrogen dioxide are next run in from a small closed vessel connected with the generating flask and the mixed liquid is then shaken, at first gently, and afterwards vigorously. The tube leading from the flask to the azotometer should be provided with a stop-cock, which should be closed before and opened immediately after each shaking.

The last trace of the oxygen liberated will not be disengaged until after the lapse of about five minutes, but it is not necessary to continue the shaking during the whole of this period. After

equalizing the height of the water in the two tubes of the azotometer, the volume of oxygen is noted and is easily corrected for temperature and pressure by reference to proper tables.

In order to test the strength of the dichromate solution by means of iron wire, a given weight of the wire is dissolved in dilute sulphuric acid, the solution reduced with zinc, as usual, and rapidly transferred to the generating flask (filtering, if necessary).

An excess of dichromate solution is now run in, hydrogen dioxide is added, and the oxygen is set free and collected as before described.

If a large excess of dichromate has been used in the preliminary test, duplicate tests should be madê with employment of a small excess, say from two to three cc., of the dichromate.

The strength of the solution can then be readily calculated by difference, and, if necessary, the results can be checked by still further tests.

In the determination of iron in ores by this process, the solutions of ferric iron are reduced by zinc, as in the common permanganate method, and the remainder of the process is conducted just as described for the standardization of the dichromate by means of iron wire.

In addition to numerous tests of solutions of pure iron, several estimations of iron in iron ores were made by this process, the results obtained being compared with those secured by the permanganate method.

The following are the results of the tests of the iron ores referred to:

	Permanganate method. Mean of several determinations.	Dichromate method.
Iron ore No. 1	40.92	40.59
		41.25
		55.35
Iron ore No. 2	54.71	55.43
		55.50

In the determination of iron in ores by this process, it is best, as in the case of the tests with iron wire, to employ only a small excess of the dichromate solution, after making a preliminary determination, as the results are much more accurate with a small than with a large excess of chromic acid.

While a sufficient number of determinations have not been made to ascertain the probable value of this method as an independent process for the estimation of iron, nevertheless some of the results secured would seem to warrant the conclusion that it might prove of utility as a check method, it being easy of execution and not at all time-consuming.

The following equation represents the changes which take place when the dichromate is brought in contact with the iron solution after reduction :

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

The writer has also attempted to apply the principle of the chromic acid method above described to the estimation of invert sugar, or rather to the determination of the amount of cuprous oxide thrown down from Fehling's solution in the process commonly employed for estimating reducing sugars.

The following equation represents the changes which take place when cuprous oxide is brought in contact with potassium dichromate in the presence of dilute sulphuric acid :

$$3Cu_2O + K_2Cr_2O_7 + 10H_2SO_4 = 6CuSO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 10H_2O.$$

The cuprous oxide thrown down from the sugar solution under examination is brought upon an asbestos filter connected with a filter pump and thoroughly and rapidly washed with hot water. The filter and contents are next transferred to the generating flask of the apparatus before described, and after the addition of dilute sulphuric acid, an excess of dichromate is run in.

Very thorough and long continued agitation of the contents of the flask is necessary in order to effect the complete oxidation and solution of the cuprous oxide, and the hydrogen peroxide must not be added until the solution is complete.

The oxygen liberated on the addition of the hydrogen dioxide is collected and the volume noted as before described. The equivalent amounts of chromic acid, cuprous oxide and invert sugar can be easily calculated from the data thus secured.

This method, while apparently satisfactory from a theoretical

standpoint, has so far failed to give sufficiently uniform results, one of the chief objections to the process being the difficulty attendant upon the solution of the cuprous oxide.

With improvements in the details of manipulation of the process, however, it is quite possible that more satisfactory results could be obtained.

SECOND INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

BY H. W. WILEY.

Received September 15, 1896.

At the first congress held in Brussels, in 1894, it was decided to hold the meetings bi-annually and Paris was selected as the most desirable place for the reunion this year. As has already been announced to the readers of the Journal, the present congress is organized under the patronage of the French government and under the immediate direction of l'Association des Chimistes de Sucrerie et de Distillerie de France et des Colonies. The late Professor Pasteur had accepted the honorary presidency of the congress, and all delegates from foreign countries have felt an especial regret that his death has prevented them from listening to his words of welcome and from forming his personal acquaintance.

To promote the interests of the congress, committees were organized in most countries. The personnel of the one in the United States has already been published in this Journal. Through the French Foreign Office all the principal governments were invited to send delegates to the congress. Official representatives were present from Belgium, Germany, Italy, Russia, Switzerland, Austria, Portugal, Denmark, and the United States. So far as I can learn, and the fact is worthy of remark, there is no representative in attendance from England, either official or otherwise. The official delegate from the United States is Mr. C. A. Doremus, of New York, while the writer has a commission as a delegate from the Department of Agriculture, and one from the American Chemical Society, sent through the courtesy of the president and council. Belgium has the largest representation of any foreign country, and, since these gentlemen are all French in their language, the congress, as is natural, is essentially French.

The congress was formally opened July 27, at 10 A. M., in the grand amphitheater of the Sorbonne. Perhaps there is no other spot in the whole world so well suited by its history and tradi-

tions for the seat of a scientific congress, especially of chemistry. In or near the Sorbonne were made those advances in chemical science which have made famous the names of Lavoisier, Chevreul, Dumas, Deville, Wurtz, Pasteur, Berthelot, and many others scarcely less renowned. The address of welcome was fitly made by Mr. Berthelot, rendered, by the death of Pasteur, the head and front of French science. The response was pronounced by Mr. Lindet, provisional president. After these addresses, the provisional secretary of the congress presented a report showing the activity of the French and other committees and giving the number of chemists who had become members of the congress.

The congress is organized with ten sections, as follows:

1re Section.—Sucrerie.

2e Section.—Industries de la fermentation: alcools, vins, bières, cidres, vinaigres.

3e Section.—Industries agricoles: laiterie, fromagerie, féculerie, amidonnerie, glucoserie, matières alimentaires.

4e Section.—Chimie agricole: engrais, terres, eaux résiduaires; alimentation du bétail.

5e Section.—Analyses officielles et commerciales des matières soumises à l'impôt.—Appareils de précision.

6e Section.—Industries chimiques: produits chimiques, pharmaceutiques; corps gras, caoutchouc, matières colorantes, papiers, tannerie, verrerie, céramique, etc.

7e Section.—Photographie.

8e Section.—Métallurgie, mines, explosifs, etc.

9e Section.—Chimie Appliquée à la médecine, à la toxicologie, à la pharmacie, à l'hygiene et à l'alimentation. Matières alimentaires: altérations et falsifications.

10e Section.—Électricité: électro-chimie.

The meetings of the congress are held in the Hôtel de la Société d'Encouragement de l'Industrie Nationale, 44 rue de Rennes, opposite the church of St. Germains des Prés and in the Hôtel des Sociétés Savantes, situated in rue Serpente, opposite rue Danton. Only four or five of the sections are in session at any one time, thus affording an opportunity to the members of the congress of attaching themselves to several sections.

In the afternoon of the first day visits were made to the Gobelin tapestries, the Museum of Natural History, botanical gardens, the National Tobacco Factory, and the Eiffel tower, the latter being reached by boats on the Seine. At the end of these visits a banquet was served on the first floor of the tower and from the tables a pleasing vision of Paris by night was obtained.

On the second day of the congress, an interesting paper was read by Mr. Moissan on the electric furnace. A large number

of samples of the typical compounds obtained at the intense heat of the furnace was exhibited and a description of their physical and chemical properties given. The possibilities of the electric furnace in the near future were outlined. Mr. Moissan described in some detail the construction of the furnace. It is best made by carving a block of quicklime into the proper shape. The high infusibility of the quicklime and its non-conducting power are points in its favor. The electrodes should be of the purest carbon and there should be no deflection of the arc into the crucible. The control of the current is of the greatest importance. For instance, in the case of titanic oxide it is reduced to titanous oxide with a current of thirty ampères; at 300 ampères titanium nitride is produced and at 3,000 ampères titanium carbide. Many metallic carbides, as, for instance, calcium, yield a gas when moistened, but the gases are not identical. In addition to acetylene, hydrogen, marsh gas, and petroleum have been obtained, the latter from uranium carbide. This fact is of great interest in respect of the origin of natural gas and petroleum, which, by many, are supposed to be of organic derivation. In the furnace, molybdenum and manganese are capable of forming compounds similar to cast iron. Fine samples of chromium obtained in the furnace were shown and many specimens of various nitrides, carbides, and borides. Chromium oxide was reduced to metal before the audience and silica was sublimed.

In addition to Mr. Moissan's paper, a general discussion of electrolytic problems was held including electrolytic methods of preparing chlorine, chlorinated soda, and calcium carbide.

Mr. Moissan has accepted an invitation to attend the Princeton College celebration in the autumn and has made arrangements to give some lectures in the United States. Our chemists, therefore, will have an opportunity in the near future to hear him and to note the great progress which the electric furnace has made possible in the line of discoveries in mineral chemistry.

Another discussion of unusual interest was devoted to the official graduation of instruments of precision. It was the general consensus of opinion that a uniform 100 gram weight of platinum should be adopted by all countries, and that all instruments and utensils for weight and volume should be referred to this standard. The official meter was regarded by all to be the ultimate standard of instruments to measure length. Some of the members favored a standard of brass coated with gold or platinum, in order to have an ultimate standard of greater volume than the one made of platinum. The difficulty of securing brass of uniform and definite constitution was considered as an insuperable objection to this proposition.

Among the many papers of special interest read on this day only a few can be mentioned here by title, *viz.*, Application of Electro-Chemistry to the manufacture of Chemical Products, by M. Joly; The Difficult Digestibility of Sterilized Milk, by M. Laurent; Determination of Soil Elements Assimilable by Plants, by M. Garola; Plan and Installation of an Agricultural Experiment Station, by M. Soillard.

At 4 P. M. the sections were adjourned to visit the new city hall (Hotel de Ville), which has finally been completely restored from its destruction by the Commune. There the members were received by the mayor of the city (Prefet de la Seine), the chief of police and the chief of the fire department. After enjoying a delightful collation, such as the city of Paris knows so well how to prepare, we were conducted by the mayor throughout the building and had described to us the mural decorations and the various groups of statuary. In the opinion of experts, the new Hotel de Ville is quite equal in its artistic decorations to the magnificent structure so wantonly destroyed by the Communists in 1871.

On the third day of the congress sessions of the sections were held only in the morning. A communication was presented to the second section by Mr. Chas. J. Murphy, describing a new process of fermenting maize and showing the way to a more extended use of this product in the European distilleries. Before the third section was read several papers giving the latest European processes for the manufacture of starch. Mr. Grandeau, an agronomist well known in the United States, presented a communication to the fourth section on the assimilability of phosphates. Methods of analysis of phosphates, especially those applicable to phosphatic slags were discussed by Mr. Cluss, of Halle, and by many others. The Wagner method of solution in ammonium citrate, of a definite constitution, was advocated by nearly all those taking part in the discussion. A paper on the official German method of determining iron and alumina in phosphates, was presented by Dr. von Grueber. The method of E. Glaser, as modified by Jones, is the one which the German chemists regard as the most reliable. This method has already been described in the *Journal of Analytical and Applied Chemistry*, **5**, 671. It was pointed out that analysts had received an impression that E. Glaser had acknowledged that this method was unsound. This, however, is not the case, but the impression arose by reason of a critique of the method by C. Glaser, of Baltimore. Mr. E. Glaser died soon after publishing his method and it devolved on Dr. Grueber to continue his work. The modifications of the original method, as proposed by E. Glaser,

which have been accepted by the German chemists are principally those made by Jones and with which American chemists are quite familiar. The process, as conducted by the German official chemists, is as follows :

Ten grams of the sample are dissolved in twenty-five cc. hydrochloric acid, sp. gr. 1.20, and the volume completed to a half liter. Fifty cc. of this solution, corresponding to one gram of the substance, are evaporated to half that volume in a beaker, ten cc. of sulphuric acid (one part to four of water) added and the mixture shaken. 150 cc. of absolute alcohol are added, shaken, and the beaker placed aside for three hours. The deposited calcium sulphate is separated by filtration and washed with absolute alcohol. The washing is finished when ten drops of the filtrate, diluted with the same volume of water, does not become red when a drop of a solution of methyl orange is added. The alcohol from the filtrate and washings is recovered by distillation, and the residue oxidized by bromine and hydrochloric acid, a slight excess of ammonia added and heated until the excess is expelled. This operation is very important to prevent the incorporation of magnesia in the precipitate. The residual precipitate is separated by filtration, any remaining on the walls of the beaker being washed off with cold water and a rubber-tipped tube. The whole is washed on the filter with boiling water until all traces of sulphuric acid have disappeared. The precipitate is dried, ignited and weighed and consists of the phosphates of iron and alumina. One-half of the weight of the precipitate consists of the oxide of iron and alumina.

The quantity of iron is determined by reducing the iron in fifty cc. of the first solution made, by means of zinc, and titrating the amount reduced by a solution of potassium permanganate in the usual way. The quantity of iron having thus been determined, it is calculated to oxide and subtracted from half the weight of the iron and aluminum phosphates. The difference is the alumina.

The members of the photographic section were provided with an interesting program, but the writer was not able to be present, and the total absence of any reports of the meetings in any of the daily papers, or in any other accessible form, makes it impossible to give even a summary of what was accomplished. I do not think it advisable to encumber the pages of the Journal with a complete list of the papers presented, inasmuch as the presenting of the titles of the papers would fill many pages and give but little idea of the proceedings. Moreover the published program, although extensive, does not include perhaps more than half the titles of the papers presented, and I am not sufficiently acquainted with the French way of doing things to be able to

complete the list. Only one program of papers and proceedings has been printed, and that evidently is to serve for the whole congress. The French in this particular might well imitate the practice of the American Association for the Advancement of Science in providing daily programs.

Interesting communications were presented to the ninth section on food adulteration, and Mr. Doremus read a paper on the nature of the gases contained in canned goods. He showed that these gases were chiefly hydrogen and probably the hydrogen is produced by galvano-electric action in the metals of the can. In all cases where much gas was found, the sides of the can were found deeply corroded. There was no evidence in these cases of the action of ferments and in every case the sterilization of the canned goods was perfect. Mr. Thomas Taylor sent to the section a communication on the crystals of butter fat embodying the results of his observations while chief of the Division of Microscopy of the Department of Agriculture. Mr. F. Jean read a communication on the distinction between butter and margarine as determined by his instrument, the oleorefractometer. This instrument has been carefully tested in the Chemical Division of the Department of Agriculture, and while it has been found to give valuable indications it is by no means so definitely diagnostic as its inventor claims.

Before the eighth section were presented memoirs on the methods of determining sulphur, phosphorus, nickel and carbon.

The afternoon of the third day (Wednesday) was given over to a visit to the celebrated agricultural school and experiment station at Grignon. The members of the congress traveled by railway to Versailles where carriages were provided to conduct us to Grignon. Passing the palace and garden of Versailles, we entered the forest and after two miles reached a stretch of fields which for beauty and fertility are scarcely equaled in the world. The wheat and oats harvests were going on and I was impressed with the primitive methods employed. The cradle and the sickle are almost universally used, only one reaping machine being seen in a drive of ten miles. At Grignon the tourists were received by Mr. Philippar, the principal of the school, and by Mr. Deherain, the director of the station, whose name and fame are well known to all chemists, especially those engaged in agriculture in the United States.

The experimental plots of the station were explained by Mr. Deherain, and thereafter, in his laboratory, he gave a brief explanation of the charts representing the results of the experiments for many years. After leaving the experiment station, the members of the congress were driven over the farm connected with the

school and they also inspected the barns, stables, horses and herds of sheep and cows. I noticed that much of the agricultural machinery, especially the reapers, hay-rakes and plows, were of American manufacture. The college buildings are part of an old chateau which, under the first empire, belonged to one of the marshals of France. The school at Grignon is the largest and most important of the three national colleges of agriculture. The other two are established at Montpellier and Rennes respectively. Three classes of pupils are admitted; *viz.*, internes, who pay $240 a year, demi-internes, whò pay $120, and externes, who pay $80. Others known as free auditors are also admitted to all the lectures and pay $40 a year. The course of instruction lasts two years and a half and includes zoology, botany, mineralogy, agricultural geology, physics, meteorology, general and agricultural chemistry, agriculture, horticulture, arboriculture, viticulture, sylviculture, rural economy, entòmology, sericulture, apiculture, technology, agricultural legislation, hygiene and military exercises. The number of pupils admitted to each class is fixed annually by ministerial decree, and is limited also in the class of internes by the number of beds. The total number of pupils, excluding the free auditors, is about 250. On the completion of the course and passing a satisfactory examination, which shall merit at least sixty-five out of a possible 100 points, the pupil receives the diploma of the National School of Agriculture, and four-fifths of the whole number thus graduating, comprising those who have received the highest marks, are excused in time of peace from all military service, except one year.

Examinations for admission to the school are competitive and include arithmetic, algebra, geometry, trigonometry, elementary physics, chemistry, zoology, botany and geology. The chemical instruction is given by Mr. Deherain and his assistants and consists of lectures and demonstrations in general and agricultural chemistry, including the chemical study of plants, soils and fertilizers. It is evident, however, that in the short time at their disposal the students can not acquire great efficiency in chemical manipulations and in fact it is not the object of the school to train agricultural chemists, but rather to provide young men with that character of instruction which will enable them to manage with intelligence and in harmony with the most advanced teachings of science, large landed estates.

Those members of the congress who did not desire to visit Grignon were offered an alternative excursion to the nickel works of Messrs. Christofle, Bouilhet and Cie., at Saint Denis. I have not been able to secure any reports of this visit.

The fourth day of the congress, July 30, was devoted exclu-

sively to the honor of the late M. Pasteur. At 9.30 in the morning, the members assembled in the chapel of Notre Dame and placed a memorial wreath on Pasteur's coffin. The body of the illustrious savant lies in an alcove near the middle of the north side of Notre Dame, the coffin scarcely visible beneath a mountain of wreaths and crowns. Not only is the alcove in which the coffin rests full of these offerings, but they have been stored, in cart-loads, in all the adjoining alcoves. They come from individuals and learned societies from all parts of the world and from nearly every municipality in France. The coffin rests here temporarily until the tomb and monument, to be erected by popular subscription from all parts of the world, are ready. The final resting place of the body of Pasteur is to be in the court of the Pasteur Institute. With bowed heads the members of the congress marched by the coffin holding only the motionless brain whose activity has done so much to advance knowledge and benefit mankind. Thence the carriages conveyed us to the Pasteur Institute where the laboratories were inspected. A collection of many compounds of historical interest, prepared by Pasteur, was on exhibition, among which were all the tartaric acids and tartrates used by Pasteur in demonstrating molecular asymmetry as displayed by the same chemical substance having opposite relations to polarized light. A large collection of original cultures of the ferments leading to the discovery of antidotes for rabies was also on exhibition. A large number of microscopes showing the specific microbes of phthisis, cancer and diphtheria attracted general interest. In the clinical rooms we were permitted to see one of the daily inoculations with antirabic serum. About thirty patients were treated in less than half that number of minutes. About two or three cc. of serum are administered by hypodermic injection to each patient. The serum is inserted in the skin on the right or left side of the abdomen, the most convenient place on account of the infrequency of nerves. Each patient receives from ten to fifteen injections on successive days. About 150 patients are received monthly, and the treatment is entirely gratuitous. Those who are able, however, usually give generously to the funds of the institute. A large collection of rabbits, guinea pigs and dogs, serving for experimental purposes, was also inspected. We were next driven to St. Cloud and through its beautiful gardens and forests to Garches, where a delightful breakfast was served at one o'clock. After breakfast a visit was made to the stables containing the horses used to furnish the anti-diphtheritic serum. There are 120 of these and all seemed to be in perfect health. Each one of these horses has been inoculated with the diphthe-

ritic poison and the blood thereafter serves as the source of the serum. Two horses were operated on as an illustration of the method of work. A large vein in the neck of the animal is opened, a tube inserted and the blood collected in a sterilized jar. So skillfully is this accomplished that scarcely a drop of blood is lost. From four to six liters of blood are collected from each animal, when the vein is closed and the horse returned to his stall. In three or four weeks he is ready to supply another quantity of blood. The jars containing the blood are placed in a cupboard for about forty-eight hours, when, if the horse has been properly inoculated, their contents will be found sharply separated into clots and serum. The serum, which is of a light yellow color, is removed by decantation and by an ingenious apparatus, which prevents all danger of infection, is bottled in vials containing ten cc. each. One horse was shown us that had furnished in the past few years several hundred liters of serum. He appeared to be good for many hundred more. The serum thus prepared is used directly by subcutaneous injection on patients suffering from diphtheria. Every appointment in these stables was such as to impress the visitors with a new and a noble idea of science, ministering thus directly to saving life and especially the lives of children. No wonder the body of him who did so much to establish the lines of investigations which, under his immediate direction, if not by his own hands, have led to such ameliorations in the sufferings of men, lies to-day in honor in one of the most magnificent churches in the world, buried under flowers and wreaths, while the memory of his work lives immortal in the hearts of the people it has blessed.

Next was inspected the national porcelain works at Sèvres, reached after a pleasant drive from Garches. The officials of the factory received the guests at the entrance and dividing the visitors into small parties each was personally conducted through the works. Beginning with the crude materials, kaolin, quartz, etc., the methods of grinding and mixing were first explained. The character of the mixing is of course suited to the nature of the object in view, the massive urns and vases having a different proportion of the several ingredients from the delicate cups and saucers. The molding of the objects was shown in detail in its three forms; *viz.*, by carving the solid moist mass, by allowing it in a pasty state to flow into moulds, and by turning the waxy mass on a table and imparting the desired form by the hands of the operator. The urns and vases are made by the first and third methods, while the thinner vessels, such as cups, etc., are made by the second method. After drying, the glaze is applied by dipping the objects in a creamy bath of the silicates serving

to form the glaze. After the glazing is fixed by firing, the objects are passed to the decorating room to receive their final colorings. After each color is applied, it is fixed by firing. The ingenious hoods used to secure an even firing of the objects were exhibited and the manner of using them shown. The construction of the large furnaces where hundreds of vases and other objects are fired at once, was described, and the furnaces cold and in action exhibited. The visit concluded with an inspection of the museum and salesrooms with their artistic and costly contents. These are known to all visitors, but the process of manufacture which was so minutely shown us is not open to the public in general. The day was finished by a drive back to Paris through the parks of Meudon and Boulogne.

Having taken the whole of the fourth day for the interesting and instructive excursions which have just been briefly described, the fifth day, Friday, July 31, was wholly devoted to the scientific work of the congress. Sections 1, 2, 4, 5, 9, and 10 held morning sessions, and 2, 3, 5, 6, 8, and 9 met in the afternoon. The time of Section 1 was devoted to a discussion of the crystallization of sugars and the methods of suppressing the molasses in the manufacture of sugar from canes and beets. The papers presented and the discussions thereon were more technical than chemical.

In the second section, the difficulties attending the detection and estimation of the higher alcohols, aldehydes and ethers in brandies and whiskies were set forth and Mr. Tavildaroff, of St. Petersburg, gave a résumé of the best methods of procedure.

In the third section the methods of determining phosphoric acid in soils and fertilizers were again the subject of discussion and papers on this subject were presented by Messrs. Garola and Sidersky. Mr. Lasne presented a résumé of his work on the detection and estimation of iron and alumina in phosphates. In section 5, papers on the analysis of fats, estimation of acetic acid in pyroligneous acid, a new method of estimating alcohol by means of the ebullioscope, and a rapid method of analyzing denaturalized alcohol were presented by Messrs. Jean, Kestner, Wiley, and Guillier, respectively.

In the ninth section, the application of the spectroscope in medico-legal cases was discussed. In connection with a discussion of the influence exerted by ptomaines on the detection of alkaloids in medico-legal cases, Mr. Doremus presented a paper entitled "Recovery of Morphine from a Cadaver Embalmed with Arsenical Solution."

The subject of the possible detection of toxines in potable

waters was also discussed and the influence exerted on them by organic matters in process of decomposition pointed out.

In the afternoon, in section 2, a paper was presented by Mr. Kayser on the properties of yeasts of different origin. A subject of interest to the wine growers of our southern states and California was a paper on the vinification in warm climates, by Mr. Dugast. The pasteurization of wines was discussed in a paper by Mr. Malvezin. Other papers of interest to wine makers were presented and discussed.

To chemists and bacteriologists engaged in the manufacture and study of butter and cheese, the proceedings in section 3 were of great interest. The best methods of disinfecting stables and creameries by chemical means were presented by Mr. Bordas. A résumé of our knowledge concerning the influence of food on the composition and character of milk and butter was presented by Mr. Martin. A general discussion of the best means of providing cities with pure milk was led by Mr. Saillard. The importance of selecting ferments in the manufacture of butter and cheese was discussed by the section, but the work done by Conn and others in the United States did not seem to be appreciated.

In section 3 a paper on the effect of impurities on the properties of metals was presented by Mr. Le Verrier, and the methods of micrographic and photomicrographic examination of metals and alloys were described by Mr. Osmond.

In section 5, Mr. Jobin presented a paper giving the data for comparing the different saccharimetric scales in use in the determination of sugar by the polariscope, and the method of securing a uniform scale was discussed by Mr. Sidersky. It was voted that a quartz plate of exactly one millimeter thickness was the most scientific standard by which to measure or fix a saccharimetric scale. The most probable value of this standard at the present time is expressed by an angular rotation of $21° 40'$.

In section 8, papers were read by Mr. Lasne on the phosphate industry, by Mr. Th. Schloesing on the condensation of vapors at a high temperature, on the ammonia industry by Mr. Truchot, and several other papers of less importance.

In section 9, the subject of the analysis of urine and the determination of urea was discussed by Messrs. Monfet, Taffe, Hodencq, Vicario, Hugnei, Barthe, Girard, and Doremus, the latter describing an apparatus for the purpose, invented some time ago by himself, and also the use of bromine dissolved in sodium bromide, as proposed by Rice.

In the evening a lecture was given to the congress in the amphitheatre of the Sorbonne on color photography by Mr.

Lippmann, who has achieved an international reputation by his researches into this important process. The principles of color photography were described and illustrated by apt experiments in conjunction with a projecting lantern. The process developed by Lippmann is based on the well known properties of thin films, as, for instance, a soap bubble to show colored bands due to the relation between the thickness of the film and the length of the waves of light. Mr. Lippmann has succeeded in depositing on a glass plate superimposed films of silver of extreme tenuousness and each of these films differs in thickness for each variation of color in the object producing the photograph. When the photograph is thus constructed it happens that when it is viewed by reflected light, every color of the object photographed is exactly reproduced. A large number of these photographs, representing paintings, flowers, landscapes and persons, was projected by reflection with the most vivid verisimilitude. Perhaps the most interesting of these was the spectrum of argon, in which the blue bands were shown in perfectly natural colors and clearly defined. The photographic effect is secured by exposing a perfectly transparent sensitive plate, backed by metallic mercury, in contact with the film. The sensitive surface of the plate is turned away from the object to be photographed. The plate holder for this operation was shown and is remarkable alike for its ingenuity and simplicity. The importance of color photography, as a means of fixing objects for study, is as great as its usefulness will prove to be in preserving with all the tints of vitality the faces of friends and the beguilements of beauty.

Mr. Lippmann kindly granted to Mr. Doremus and myself a private interview after the lecture, where we had a better opportunity to examine the negatives. They resemble the daguerreotypes of forty years ago and a distinct view of the image is only obtained by inclining the plate in the proper manner to secure the reflection of the light. Unfortunately, these negatives are not capable of being reproduced as positives as in the case of ordinary photography, and we are apparently as far away as ever from multiple printing color photography.

Sixth day, Saturday, August 1. Sessions of the sections were held only in the morning and those meeting were 1, 2, 4, 6, 7, 8 and 10.

In the fourth section Mr. Kjeldahl gave a brief statement of the present methods of conducting his process for the determination of nitrogen by moist combustion. Papers on methods of detecting and preventing frauds in the sale of commercial fertilizers were presented by Mr. Petermann. A paper on the importance of international agreement in methods of agricultural

analysis was presented by the writer. A general discussion of official methods of analyzing fertilizers was carried on, and at the end it was voted that the congress collect and publish in German and French the official methods of France, Germany and the United States. Mr. Sidersky was selected as editor of this brochure.

Messrs. Roy and Jean gave a paper in section 6 on tannins, their nature and analysis. It contained little that is new to American chemists and showed a lack of familiarity with the American publications on that subject.

In section 7 Mr. Vogel presented a paper on photography in colors, and one on the same subject was presented by Mr. Vidal. These papers gave in detail the points given *en résumé* in Mr. Lippmann's lecture.

In section 9, Mr. Guichard read a paper on alcohol from a hygienic point of view.

The employment of aluminum in the construction of cooking utensils and its influence on the wholesomeness of food prepared therein was the subject of a paper by Mr. Boroma. It was shown that with proper precautions aluminum could be safely used, but that it presented few if any advantages over copper or other metals in common use.

So widely has aluminum come into use for cooking utensils that a brief abstract of our present knowledge concerning its merits may be presented. The utility of an aluminum dish, in respect to its fitness for culinary vessels, depends on the purity of the metal. A pure aluminum dish is almost if not quite as resistant to solvent effects of ordinary foods as any common metal. The impurities which do the most harm are sodium and carbon. When the aluminum contains carbon an electric current is at once set up when a suitable liquid is applied. In such cases after water, especially if it be saline, has stood in the dish for one or two weeks, the surface will be found dotted with brilliant rings, and on scraping off the aluminum the particle of carbon will be disclosed. If a strong solution of salt be used, the action may be sufficient to cause a perforation of the metal. The aluminum of commerce, unfortunately, is not very pure, and it is for this reason that so many aluminum dishes have shown a rapid deterioration. The French troops in Madagascar have been supplied with 15,000 sets of aluminum dishes, and, when a soldier has to carry his kitchen with him, the importance of lightness is not to be despised. But even granting that in cooking in aluminum dishes a small amount of alumina is introduced into the food, it has not been shown that it exercises the least harmful action on the digestion. The experience of two men

may be cited who lived for a year on food prepared exclusively in aluminum dishes without the slightest impairment of their health.

In the afternoon the members were driven in carriages to Gennevilliers, where they inspected the irrigation works, lately constructed to supplement those at Asniéres in disposing of the sewage of Paris. It has now been more than a quarter of a century since the city of Paris has been using its sewage for irrigation. The fact that in the light of that long experiment it has recently more than doubled the area under irrigation, shows that the process is considered a practical success. The sewage of Paris consists mostly of the water used for washing the streets. Water-closets are, to a large extent, connected with vaults whose contents are removed by means of wagons, pumps and closed tanks during the night. The sewage, therefore, is not so highly polluted nor so rich in fertilizing materials as might have been supposed. For summers like the present one, which has been excessively dry, the disposal of the sewage by irrigation is easily accomplished. But in summers of excessive rainfall and in the winter, the problem is much more complex.

We first were shown a plan on a large chart of the system of sewers and the distribution of the waters. Next the pumping house was visited where the sewage is raised to a sufficient height to carry it under the Seine by a siphon aqueduct and distributed to the irrigated fields. The fields which were inspected are only a part of the vast system of irrigation now in operation. They contain 799 hectares, a part of which was once covered by the old forest of St. Germain. The city of Paris spent 200,000,000 francs in the purchase of the grounds, the building of the aqueduct, erecting the pumping machinery and building the irrigating canals. The work on the aqueduct of Achéres was commenced in 1893 and the whole work was completed in 1895. The aqueduct is eleven kilometers long and is three meters interior diameter, and it crosses the Seine, which below Paris forms a loop, twice. Fortunately, the soil, forming the basin of the Seine in this locality, is of a sandy nature and permits a somewhat rapid filtration. A clay subsoil would render the whole process inapplicable. The gardens, though only two years old, presented a scene of almost tropical exuberance. Many dwarf fruit trees were already in bearing and older trees showed the existence of orchards before the present system was inaugurated.

The methods of irrigation are exactly those practiced in the arid regions of the United States. The water is conducted in furrows on the surface between the rows of growing crops. Aside from a slightly unpleasant odor arising from the sewage, there is nothing in the scene to cause the observer to look on

the perfect vegetables and flowers with suspicion. In harmony with the French devotion to art, the borders of all the plots are planted in roses and other flowers and these, at the time of our visit, were all in full bloom, recalling in their floral exuberance the gardens of California. Here, as a result of the applications of science, typhoid fever is turned into turnips, dysentery dances in the dew on the dahlias, and cholera comes chortling as cabbage. The one unpleasant reflection is found in the fact that this extensive harvest is sold exclusively in the Paris markets and one can hardly avoid thinking in the restaurants over his cauliflower and artichoke of the long race they may have run in the aqueduct of Achêres. At the end of the experimental field, next to the river, the sewage which has passed through the soil reappears as a large stream of pure water, absolutely colorless and bright. Glasses of the attractive fluid were offered the visitors, many of whom, unmindful of miasm and microbes, drank, willing martyrs to science or curiosity. The number of micro-organisms, which is many millions in the sewage, is diminished to 2,500 in each cubic centimeter of the filtered water.

Seventh day, Sunday, August 2. An excursion was offered to the members of the congress on Sunday to Compêigne. On reaching the station, a band of music welcomed the excursionists. They were driven through the gardens and forests in carriages and at one o'clock a breakfast was served.

Eighth day, Monday, August 3. In section 1 papers were presented on the methods of determining water in organic viscous liquids, by Mr. Pellet. The process recommended is by absorption with pumice stone and subsequent drying, first at 60° to 80° and finally at 100°. Molasses and solids should first be dissolved in water to promote absorption by the pumice. A drying dish was exhibited with a circular depression in the center, into which the body is weighed and mixed with enough water to make it flow easily. The fragments of pumice are placed on the flat bottom of the dish, exterior to the depression, and the dissolved mass is absorbed by the pumice on inclining the dish. The dish and cover are made of aluminum. The diameter of the dish is about seven and its depth two cm. The composition of molasses derived from the sugar cane was discussed at some length. Raffinose, to the extent of three per cent., has been detected in samples of cane molasses of Egyptian origin. The reducing sugar, in cane molasses, according to the statement of Pellet, is composed solely of invert sugar, a conclusion which he has reached by applying the method of estimating levulose described by the writer in this Journal a few months ago.[1]

[1] Vol. 18, No. 1, p. 81.

An interesting paper by Mr. Herzfeld, of Berlin, gave a résumé of the best methods of separating sugars in mixtures.

In section 3, the session was devoted to the chemical study of processes of bread making, and especially to the methods of analysis of moist and dry gluten. The processes presented are almost identical with those in use in the United States. Mr. Lindet, the president of the congress, read a communication on the methods of determining starch in grains and flours, in which the separation by a ferment or by water under steam pressure was recommended as the best. These are the processes which we have preferred for several years in the agricultural laboratory at Washington.

In section 6, papers were presented on gutta percha, paper, and paint used to prevent corrosion of ship bottoms.

In section 9 a paper on the analysis of wines and vinegar was presented by Mr. Leroy. The detection of glucose in beer was discussed by Mr. Padé. The question of fermentation and the germicidal methods of controlling it by means of fluorides was discussed by Mr. Effront.

An interesting exhibition was given of the workings of the latest form of bomb calorimeter for the determination of the thermal equivalents of foods.

Among the more interesting papers presented in the afternoon may be mentioned one by Mr. Fernback, director of the laboratories of the Pasteur Institute, on the utilization of the carbon dioxide arising from fermentation, in section 2; the influence of culture on the chemical and physical properties of the soil, by Mr. Deherain, in section 4, and the estimation of lactose and sucrose in condensed milks, by Mr. F. Dupont, the general secretary of the congress, in section 5.

In the evening a banquet was given to the chairmen of committees of organization and to the delegates of foreign governments, in the Salle des grandes Fêtes of the Grand Hotel, under the presidency of Mr. Cochery, Minister of Finance, at which nearly 500 sat down. An orchestra rendered beautiful music during the repast, giving among other things the national airs of the various governments represented. "Yankee Doodle" doubtless was heard with equanimity, but one can imagine the feelings of the Frenchmen present when "Die Wacht am Rhein" was given. Short addresses were made by Mr. Lindet, the president of the congress, by Mr. Doremus, on the part of the foreign delegates, and a rather long one by the Minister, who greeted the chemists for many reasons, and especially, he said, "because you are the precious auxiliaries of my department in promoting the production of articles that can be taxed." Mr. Doremus introduced his address by quoting one of the inscriptions on the statue

of Danton: "Apres le pain l'education est le plus grand besoin du peuple." He alluded to the addresses of Berthelot, Moissan, and Lippmann, as illustrations of a few of the accomplishments of applied chemistry, and said the congress had shown in a striking manner the necessity of a close alliance between applied and research science. Pasteur will owe his immortality to the great faculty he possessed of finding a practical application for his discoveries. He concluded as follows: "Hon. Minister of Finance, representing the French Republic, M. Berthelot, the illustrious president of honor of this congress, M. Lindet, the president of the congress, M. Dupont, the secretary, I wish to thank you in behalf of the foreign delegates, for the hospitality, friendship, and good fellowship with which we have been received. In the name of the foreign delegates, I propose this toast, the French Republic, patron not only of this congress, but also of science, art and industry, the mother of men famous in each science, but especially in chemistry."

The strangers present were given a very favorable opportunity to understand the heartiness of French hospitality and the excellence of French cooking. We might learn more things than good cooking from a French banquet and among others the art of limiting the post prandial speeches. At ten o'clock the guests left the table and assembled in the grand salon, where coffee and liqueurs were served and an hour or more spent in social intercourse.

Ninth day, Tuesday, August 4. I have already used so much space in giving even a few of the details of the congress that it is not advisable to mention even the more important communications presented to-day. Morning sessions only were held. In the afternoon the Conservatoire des Arts et Mêtiers was visited, where the congress was received by Mr. Aimé Girard, the professor of applied chemistry, and shown through the laboratories and museums. In the latter alone are enough objects of interest to employ the time of a scientist for a month for a careful study. We can only mention *fastigia rerum*. The pendulum used by Foucault in his classical experiments is still swinging and showing by its deflections the rotation of the earth. All the important apparatus used by Lavoisier is collected here. The globes employed by him for determining the composition of water are remarkably well made and even to-day would be regarded as entirely convenient. But they have their chief value as the remains of those era-making investigations, cut short by the guillotine, which laid the foundation of modern chemistry. A wooden wheel, preserved by the copper sulphate in an abandoned copper mine since the fifth century, illustrates in a most

striking way one of the best methods of preventing decay in railroad ties. The standard measures of all nations make an interesting collection, but, unfortunately, we were not permitted to see the original meter, which is preserved from view in the vaults of the building. In the courtyards are bronze statues of Le Blanc, who made the fortunes of so many and committed suicide by reason of his own poverty, and of Boussingault, the contemporary of Liebig and the father of French agricultural chemistry. A photographic view of the congress was made on the steps of the west façade of the building.

Tenth day, Wednesday, August 5. In the morning the sections held their final sessions for hearing papers and discussions. In the afternoon the closing meeting of the congress was held in the grand amphitheatre of the Sorbonne under the presidency of Mr. Henri Boucher, Minister of Commerce and Industry. Addresses were made by Mr. Lindet and the Minister and a report of the proceedings of the congress presented by the secretary, Mr. Dupont. Turin and Vienna were placed in nomination as the places of meeting of the congress in 1898. Vienna was selected by a large majority. An invitation was extended by Mr. Lindet to hold the congress of 1900 in Paris during the World's Exhibition, and that invitation will doubtless be accepted at Vienna.

After the adjournment of the meeting, the new laboratories of organic chemistry, constructed by Friedel, were inspected by Mr. Doremus and myself. In the confusion of the summer cleaning, we could hardly form any favorable judgment of their points of excellence. The ultra impressionist painting of Paradise Lost, a mural ornamentation back of the professor's lecture table, was the most original and inexplicable feature of the laboratory.

PARIS, August 10, 1896.

NOTE.

The fourteenth annual report of the Committee on Indexing Chemical Literature was presented to the American Association for the Advancement of Science at the Buffalo meeting, August 24. A large amount of work has been done in this field during the year. The committee is an active one and has done a valuable work in encouraging and recording biographical undertakings. Copies of the report may be obtained of the chairman, Dr. H. Carrington Bolton, Cosmos Club, Washington, D. C.

VOL. XVIII. [NOVEMBER, 1896.] NO. 11.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

A NEW FORM OF POTASH BULB.[1]

BY M. GOMBERG.

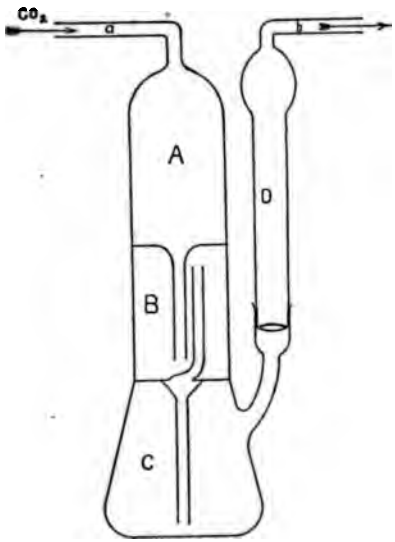
Received August 28, 1896.

THE potash bulb most frequently used at present in elementary organic analysis is that known as Geissler's bulb. While neat and compact, it still has the same drawback as possessed by other forms of potash bulbs; namely, that even with the most careful handling it is not unfrequently broken. Some two years ago I drew up a design for a different form of bulb, wherein all the connections should be enclosed. Several attempts to have it made in this country have proven unsuccessful. The design was then sent to Greiner & Friedrichs, of Thüringen, and I have recently received from them samples of such bulbs. Meanwhile, it came to my notice that a bulb based on similar principles has been put upon the market by Bender & Hobein, of München. A comparison of the two bulbs shows them, however, to be sufficiently different to justify me in presenting a description of the one made according to my design, without claiming priority as to the principle of construction.

The arrangement and working of the bulb will appear clear from the subjoined diagram, which presents the apparatus reduced to one-half its actual size.

The potash bulb is divided into three compartments, *A*, *B* and *C*. *B* and *C* contain the potash solution for the absorption of the carbon dioxide, while *A* serves as a safety reservoir in case of backward suction. The bulb is filled by dipping *a* into the solution, and applying suction at *b*, until the two com-

[1] Communicated by A. B. Prescott. Read at the meeting of the American Chemical Society, Buffalo, N. Y., August 22, 1896.



partments B and C contain as much of the solution as would completely fill A, which is about thirty-five to forty grams of a 2 : 3 solution. D, which is fastened to the bulb by means of a ground-glass joint, contains solid potassium hydroxide, or soda-lime, supported by a plug of glass-wool. The liquids in B and C can be easily mixed when desired, by applying suction at *a*. The bulb, when filled and ready for use, weighs from sixty-five to seventy grams, and undoubtedly can be made even much lighter.

The total number of compartments is thus reduced from five in Geissler's form to three in the form here presented, while the absorbing chambers are reduced only from three to two. The construction of the bulb is such that C can never get overfilled by the solution from B.

This form of a potash bulb possesses the advantages first, that it can be easily handled and wiped, presenting the outside surface of an ordinary small flask, and second, that it can be set without any support, and can be weighed without suspending it if so desired.

I wish to express my thanks to the firm of Greiner & Friedrichs, of Thüringen, who have kindly made the bulb for me in a most satisfactory manner.

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REDUCTION OF CONCENTRATED SULPHURIC ACID BY COPPER.

BY CHARLES BASKERVILLE.

Received August 27, 1896.

IN a previous communication[1] the writer noted that copper was acted upon by concentrated sulphuric acid (1.84 sp. gr.) not

[1] This Journal, 17, 90.

only at the ordinary temperatures of the air, 20°–30° C., but at zero as well. Andrews[1] states that the assertion is incorrect and that it does not occur until the temperature 86° C. has been reached, or a point above the dissociation temperature of the concentrated sulphuric acid, 67° C., according to him. Andrews further says that the author's statements were based "not upon any demonstrations of the formation of sulphurous acid, but solely on the formation of copper sulphate," which, he says, occurs only "in consequence of the presence of the air." It is to be regretted that Dr. Andrews did not note carefully the statements of the author in his previous communication, as no reason whatever exists for any such conclusions, because it was distinctly stated that not only the copper as sulphate, but as sulphide was determined, as well as sulphurous acid, and moreover, that the experiments were carried out when the air had been replaced by a neutral gas, either hydrogen or carbon dioxide.

The author, although confident of the correctness of his former statement, carried out further experiments to correct the error, if committed or to establish, beyond question, the fact that concentrated sulphuric acid of 1.84 sp. gr. is reduced by copper below 86° C., the limit *positively* set by Dr. Andrews.

The fact that these experiments but confirmed the former statement of the author allows the incorporation of the results in this paper.

As far back as 1834 the fact that copper is acted upon by concentrated sulphuric acid at ordinary temperatures, if sufficient time be given, was made known by Barruel.[2] Calvert and Johnson,[3] however, failed to obtain any action below 130° C. and considered that none took place. Pickering,[4] however, stated that "sulphuric acid attacks copper at all temperatures from 19° C., (and probably even still lower) upwards."

First Experiment.—Copper ribbon in strips, 1 x 3–4 cm., was submerged in concentrated sulphuric acid in a clean glass stoppered flask for a month. At the end of that time not only were there white crystals of anhydrous copper sulphate clinging to

1 This Journal, **18**, 253.
2 *J. de pharm.*, 20, 13, *1834*.
3 *J. Chem. Soc.*, 19, 438, *1866*.
4 *J. Chem. Soc.*, Trans., *1878*, 113.

the sides of the containing vessel, but there was a very appreciable amount of brownish black cuprous sulphide and sulphur dioxide was easily detected by its strong odor when the vessel was opened.

Andrews[1] states "that in the presence of air sulphuric acid is attacked by copper at ordinary temperatures, but without reduction of the acid. The reaction must take place according to the equation,

$$2Cu + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O."$$

Formerly the author[2] stated that the presence of the oxygen of the air when it comes into contact with the copper in the acid has great influence on the reaction. Fifty years ago, Maumené[3] proved that when a current of oxygen gas was passed through the boiling acid, the amount of insoluble residue, *e. g.*, cuprous sulphide, was diminished, that is, less than there would be formed if the experiment were carried out with a current of carbon dioxide. The copper must be directly exposed to the oxygen by only partial submersion or the bubbling of the air against or around the submerged copper; but the air in a confined space, not at all in contact with the copper, but separated by a thick layer of concentrated sulphuric acid, has little or no effect.

Yet grant that the oxygen of the air (volume of air about 200 cc.) confined in the flask, had been utilized in the formation of the copper sulphate produced. According to the formula given above, the oxygen would be absorbed and no corresponding amount of any other gas would be eliminated; consequently there should be a greater external pressure at the close than at the beginning of the experiment. When the smoothly fitting glass stopper was removed, not only no extra internal pressure was noticed, but in fact a pressure from within. This was evidently produced by the sulphur dioxide generated. The sulphur dioxide was swept out by a current of air through a dilute solution of potassium permanganate, which was quickly bleached. The presence of sulphur dioxide was further proven by the addition of barium chloride to the bleached potassium permanganate

1 This Journal, 18, 252.
2 *Ibid*, 17, 912.
3 *Ann. chim. phys.*, *1846*, [3], 18, 311.

solution. Nor does the formula given above account for the cuprous sulphide which is always produced.

Second Experiment.—Realizing the possibility of some organic matter or dust remaining in the flask, although it had been carefully cleansed, the first experiment was repeated with the greatest precaution to ensure the absence of dust. The flask was scoured with boiling concentrated pure sulphuric acid containing potassium bichromate and carefully cleansed with distilled water. The last traces of water were removed by four subsequent washings with the same kind of concentrated acid used throughout the experiments. The experiment was carried out in the same manner as the first, the same results being obtained.

A blank experiment was carried out at the same time. The flask was rendered dust free in the manner just mentioned and fifty cc. of the same acid allowed to remain in the flask for six months. At the end of that period not a trace of sulphur dioxide could be detected in the blank, therefore the sulphur dioxide produced when the copper was inserted could not be due to the reduction of the sulphuric acid by an extraneous substance, but solely by the copper. The conclusion is that sulphuric acid is reduced by copper when air is present at the ordinary temperatures, 20°–30° C.

Third Experiment.—An ordinary Kjeldahl digestion flask was made dust free by the treatment noted above. 100 cc. sulphuric acid, 1.84 sp. gr., were placed therein and clean dry strips of copper ribbon were completely submerged in the acid. Now air-free carbon dioxide was passed through the flask for three hours. The inlet tube was just dipped into the acid. The flask was then attached to a suction pump, with a sulphuric acid drying flask intervening to prevent a possible return flow of gas or air which might carry moisture or dust into the flask. The flask was exhausted of the carbon dioxide present for three hours at a pressure of 150 mm. It was then sealed with the blast lamp and placed aside in a darkened cupboard. Observations were made every few days to note any reaction taking place. Within two days it could be easily seen that copper sulphate had been formed and the liquid was somewhat clouded by very finely divided suspended cuprous sulphide. Continued

observations extending over a period of seven weeks showed only an increase in the amounts of both of these substances. The temperature of the cupboard had at no time risen above 20° C., and was for most of the time much lower. The flask was then opened as any other sealed tube, and instead of an external pressure inward, which had been sufficient to heavily dent the tube in sealing, there was a strong internal pressure outward. The gas evolved was sulphur dioxide, easily detected by its strong odor and bleaching effect upon a dilute solution of potassium permanganate. The sulphuric acid produced by the oxidation of the sulphur dioxide by the permanganate was precipitated by barium chloride. All solutions and apparatus were proven to be free from traces of sulphur dioxide and sulphuric acid by a blank experiment.

Conclusion.—Concentrated sulphuric acid, 1.84 sp. gr., is reduced by copper when air is absent and at temperatures far below 86° C., in fact at the ordinary atmospheric temperatures with the formation of copper sulphate and cuprous sulphide and the production of sulphur dioxide.

Finally.—Apparatus similar to that made use of by Andrews[1] was employed with the modification of having three drying flasks containing concentrated sulphuric acid instead of one, and a Meyer absorption tube was substituted for a single small flask. These served merely as extra precautions against dust and insured an intimate mixing of the outgoing gases with the permanganate. Within twelve hours the permanganate was bleached. Andrews' experiment lasted only fifteen minutes. The presence of the sulphur dioxide produced was easily detected by the odor when the apparatus was opened, and in the bleached permanganate solution by barium chloride. Copper sulphate and cuprous sulphide were also formed.

Concentrated Sulphuric Acid is Acted upon by Copper at Zero.—Quantitative experiments were carried out by the author when the concentrated sulphuric acid in which the copper was submerged was practically at zero.[2] In stating the results, however, the author gave the temperature as "0°–10° C." The flask

[1] This Journal, 18, 251.
[2] *Ibid.*, 17, 908.

containing the acid was buried in an ice-bath and the temperature of the liquid noted by a thermometer inserted through a rubber stopper. The apparatus was air-tight. A stream of hydrogen gas was continued through the apparatus in one experiment for six weeks and in another two months. On two occasions when the ice in the bath had melted in going over Sunday, the temperature rose to 10° C. The temperature could not possibly have remained that high for over twelve hours, which would have had small influence when the experiments lasted through a number of days. The temperature was reported 0°-10° C., however. Not only copper sulphate, but cuprous sulphide and sulphur dioxide had also formed. Copper, therefore, decomposes concentrated sulphuric acid (sp. gr. 1.84) practically at zero.

From my own experiments and from experiments performed with apparatus similar to that used by Andrews and under the same conditions, except with regard to the important element, time, which consideration is necessary for all chemical reactions, the author must adhere to his former statement.

UNIVERSITY OF NORTH CAROLINA.

THE SEPARATION OF THORIUM FROM THE OTHER RARE EARTHS BY MEANS OF POTASSIUM TRINITRIDE.

BY L. M. DENNIS.

Received September 4, 1896.

SOME time ago the author and F. L. Kortright[1] briefly described the action of a solution of potassium trinitride upon a neutral solution of the rare earths. It was found at that time that the flocculent precipitate which is produced was most probably thorium hydroxide, but our supply of potassium trinitride having been exhausted it was impossible to further investigate the reaction or ascertain the completeness of the separation. The immediate continuation of the work was prevented by unexpected difficulties which were encountered in the preparation of pure hydronitric acid on a large scale. These difficulties have since been removed, and it has been possible to prepare an amount of the reagent sufficient for the investigation described below.

[1] *Ztschr. anorg. Chem.*, 6, 35; *Am. Chem. J.*, 16, 79.

The solution of potassium trinitride which was used was prepared by carefully neutralizing a dilute solution of hydronitric acid with a dilute solution of pure caustic potash and then adding hydronitric acid sufficient to give to the solution a distinctly acid reaction. The solution first employed contained about three and two-tenths grams of potassium trinitride to the liter.

Before studying the separation of thorium from the other rare earths, the reaction between potassium trinitride and pure thorium chloride was first investigated. The thorium employed was from a sample of thorium oxalate, which had been very kindly presented to me by Dr. Theodor Schuchardt, of Goerlitz. It was found to be of a very high grade of purity, but to guard against the possible presence of other rare earths, the oxalate was converted to the oxide by ignition, treated with concentrated sulphuric acid, the anhydrous sulphate dissolved in distilled water at a temperature of 0°, and this solution was precipitated with pure oxalic acid. The precipitated thorium oxalate was thoroughly washed with hot water containing one per cent. hydrochloric acid, and was then dropped into a hot, concentrated solution of ammonium oxalate. It dissolved completely and no precipitate formed when the solution was diluted and cooled. From this solution the thorium was again precipitated as oxalate by means of strong hydrochloric acid and was then brought into solution as thorium sulphate in the manner described above. It was then precipitated by ammonium hydroxide and the precipitate thoroughly washed with water. The thorium hydroxide was then dissolved in hydrochloric acid, ammonium hydroxide was added until a faint but permanent precipitate remained, and this was then removed by filtration. There was thus obtained a neutral solution of thorium chloride containing a very small amount of ammonium chloride.

The strength of this solution of thorium chloride was ascertained by precipitating portions of ten cc. each with ammonium hydroxide, filtering, washing, igniting, and weighing as ThO_2. Two determinations gave, for thorium oxide in ten cc., 0.0591 gram and 0.0595 gram. The mean of these results is equivalent to 0.00521 gram thorium in one cc.

Upon adding to this thorium solution a few cc. of the solution

of potassium trinitride, the precipitate which, in the previous work with Dr. Kortright, had formed at once, failed to appear; upon heating the solution to boiling, however, there was quickly formed a white, flocculent precipitate, closely resembling in appearance aluminum hydroxide, but settling rapidly when the flame was removed. In the first determinations the solution was boiled for five minutes, but it was later found that boiling for one minute is sufficient. During the boiling the odor of hydronitric acid was distinctly noticeable. The precipitate was washed by decantation with hot water, transferred to the filter, ignited, and weighed as ThO_2. Twenty cc. of thorium chloride, containing, according to the determination with ammonium hydroxide, 0.1186 gram thorium dioxide gave, by precipitation with potassium trinitride, 0.1183 gram thorium dioxide, equivalent to 0.00520 gram thorium in one cc. instead of 0.00521 as obtained with ammonia.

It is apparent, therefore, that thorium can be quantitatively precipitated by potassium trinitride.

The previous work of Dr. Kortright showed that the thorium is probably precipitated as the hydroxide, but the tendency of the precipitate to absorb carbon dioxide rendered the analyses unsatisfactory. If, however, the thorium is precipitated as the hydroxide, then all of the hydronitric acid of the potassium salt first added must reappear in the filtrate from the thorium hydroxide and in the gas evolved during the boiling. To ascertain whether this took place the precipitation was made in a round bottomed flask. In the neck of the flask there was inserted a two hole rubber stopper, through one opening of which a current of purified air was admitted, the other opening carrying an upright condenser. The condenser was connected at the upper end with two absorption vessels containing neutral silver nitrate solution. As the hydronitric acid was to be determined by precipitation with silver nitrate, a neutral thorium nitrate solution, containing 0.0075 gram thorium in one cc., was substituted for the thorium chloride. The thorium nitrate solution was placed in the flask, potassium trinitride was added, and after starting a current of air through the apparatus, the contents of the flask was heated to boiling and kept boiling for two

minutes. Soon after the heating began a white precipitate of silver hydronitride formed in the first absorption flask containing the silver nitrate; by the time the reaction was complete this precipitate had become quite voluminous. The absorption of the gas by silver nitrate seems to be both rapid and complete, for nothing more than a slight opalescence ever appeared in the second absorption flask. After the apparatus had become cool the thorium hydroxide was filtered off and the filtrate was precipitated by silver nitrate. The silver trinitride thus obtained, together with that in the absorption flasks, was washed by decantation with cold water, the washings being passed through a hardened filter. When the wash water gave no further reaction for silver the funnel with the filter was placed in the neck of the flask containing the main part of the precipitate, and quite dilute, hot nitric acid was poured upon the paper. The silver trinitride on the paper dissolves almost immediately. After washing the paper with water, the funnel was removed and the contents of the flask was boiled until all of the silver trinitride had dissolved. The silver was then precipitated by hydrochloric acid and weighed as silver chloride. Ten cc. of thorium nitrate and ten cc. of potassium trinitride were used. The silver chloride resulting weighed 0.1447 gram, equivalent to 0.0434 gram hydronitric acid. The strength of the potassium hydronitride, which was a different solution from the one first employed, was then determined in the same manner.

$$5 \text{ cc. gave } 0.0744 \text{ AgCl} = 0.02232 \text{ } HN_3,$$
$$5 \text{ cc. gave } 0.0745 \text{ AgCl} = 0.02235 \text{ } HN_3.$$

Using the mean of these results, it appears that 0.0446 gram of hydronitric acid was used in the precipitation of the thorium nitrate, of which 0.0434 gram was recovered from the filtrate and distillate. That this latter result is somewhat low is doubtless due to the loss of hydronitric acid by volatilization during the filtration of the liquid in the flask. These results, together with those given in the preceding article already referred to, enable us to represent the reaction by the equation

$$Th(NO_3)_4 + 4KN_3 + 4H_2O = Th(OH)_4 + 4KNO_3 + 4HN_3.$$

This reaction is interesting not only because of the quantita-

tive precipitation of thorium by this means, but also because of the peculiar behavior of the potassium hydronitride. As Ostwald has stated, hydronitric acid is but slightly stronger than glacial acetic acid, and the above equation reminds one of the behavior of acetates towards ferric iron, the solution of ferric acetate being fairly stable in the cold, but breaking down upon heating, into acetic acid and ferric hydroxide.

The experiments detailed below were then made to ascertain whether thorium could be quantitatively separated from the other rare earths by means of the above reaction. A neutral solution of pure lanthanum chloride was first prepared and its strength determined by precipitating with ammonium hydroxide and weighing the lanthanum as La_2O_3. The solution contained 0.00431 gram lanthanum in one cc. This solution gave no precipitate when boiled for some minutes with potassium trinitride. Fifteen cc. of this solution and fifteen cc. of the thorium chloride solution were placed in an Erlenmeyer flask, twenty-five cc. of potassium trinitride (three and two-tenths grams to the liter) was added and the solution was boiled for one minute. The precipitate was filtered off and washed with hot water, ignited, and weighed. To the filtrate five cc. more of potassium trinitride was added and the solution boiled for two minutes. No further precipitation resulted. The solution was then precipitated with ammonia and the lanthanum weighed as the oxide. The results were:

	Taken.	Found.
Thorium	0.0781	0.0777
Lanthanum	0.0646	0.0642

A mixture of the rare earths in Brazilian monazite was then freed from thorium by repeatedly digesting the mixed oxalates with a hot, concentrated solution of ammonium oxalate. The residual oxalates were then transformed into chlorides and dissolved in water. The solution showed the pink color and absorption bands of didymium and gave a strong reaction for cerium when treated with hydrogen peroxide and ammonia. When boiled with potassium trinitride it gave a very faint precipitate which was filtered off. By precipitation with ammonia this solution of cerium, lanthanum, didymium, etc., free from

thorium, was found to contain 0.0166 gram of the mixed oxides in one cc. The precipitation was made as in the separation from lanthanum and an excess of potassium trinitride was used in each case.

		Taken.	Found.
I.	Thorium	0.1300	0.1294
	Ce, La, Di oxides	0.0332	....
II.	Thorium	0.0785	0.0783
	Ce, La, Di oxides	0.0830	....
III.	Thorium	0.0535	0.0526
	Ce, La, Di oxides	0.2490	....
IV.	Thorium	0.0535	0.0531
	Ce, La, Di oxides	0.2490	....
V.	Thorium	0.0550	0.0541
	Ce, La, Di oxides	0.4980	....
VI.	Thorium	0.0555	0.0550
	Ce, La, Di oxides	0.5810	....
VII.	Thorium	0.0570	0.0558
	Ce, La, Di oxides	0.8300	....

The recovery of the thorium is in all cases fairly exact and the variation in the relative amounts of thorium and the other earths does not influence the sharpness of the separation. That thorium alone is precipitated by potassium trinitride is to be explained by its weak basicity. It is the weakest base in the whole group of the rare earths with the possible exception of cerium in the ceric condition, and this higher form of cerium is probably incapable of existence in the presence of hydronitric acid.

We have, then, in potassium trinitride a reagent which can be used both for the qualitative detection of thorium and for its quantitative determination either alone or in the presence of other rare earths. So far as the author is aware, this is the only method as yet devised by which one of these earths can be quickly and accurately separated from the others, and that in a single simple operation.

CORNELL UNIVERSITY, August, 1896.

NOTES ON REINSCH'S TEST FOR ARSENIC AND ANTIMONY.

By Jas. Lewis Howe and Paul S. Mertins.

Received September 12, 1896.

THAT Reinsch's test for arsenic possesses, in point of convenience, marked advantages over that of Marsh, is generally acknowledged, but it has been questioned both as to delicacy and as to accuracy in distinguishing between arsenic and antimony. As to the former point, Reinsch, in his second article on the test,[1] states that arsenic may be detected in a solution of one part per million. In his original description[2] of the test he placed the accuracy about one-third of this. Our own experiments show that this accuracy is not overstated. The fact that arsenious oxide and antimonous oxide (Sb_2O_3) are isomorphous in their crystallization has led to the conjecture that antimonous oxide subliming from the copper in the closed tube might appear in the brilliant octahedra, characteristic of arsenic in the test.

Experiments bearing on this point were made as follows:

Reinsch's test was applied to the different compounds of arsenic in this laboratory and in each case several sublimation tubes were used. The test was carried out by boiling the substance with sixteen per cent. hydrochloric acid, in which several strips (2.5×0.5 cm.) of thin, pure copper were placed. After fifteen minutes (except in cases to be mentioned later) the strips of copper were removed, washed and dried, and after rolling or folding to small compass, placed in open tubes five cm. long and not over five-tenths cm. diameter. These tubes were held in an inclined position in the lowest possible flame of a Bunsen burner until the arsenic sublimed; a second or two usually suffices.

The test was similarly carried out with compounds of antimony and also with various organs of two cats, one killed by six grains of tartar emetic, dying six hours after administration, and the other dying in three days after the administration of the first of six small doses given every twelve hours. Each dose was two grains, but much of this was probably not taken into the system. A perceptibly higher degree of heat was necessary to

[1] H. Reinsch: De l' Essai de l' Arsenic par le Cuivre: *J. pharm. Chim.*, 2, 361, (*1842*).

[2] H. Reinsch: Ueber das Verhalten des metallischen Kupfers zu einigen Metalllösungen: *J. prakt. Chem.*, 24, 244, (*1842*).

sublime the antimony than was the case with arsenic; altogether 185 tests were made, most of them furnishing good sublimation tubes. Each tube was numbered as made, and later the whole number were mixed and sorted for arsenic and antimony by examination with a microscope of low power. Reference to the note book showed that in no case had a mistake been made, in fact in every case the arsenic sublimation could easily be distinguished from that of antimony by the naked eye. In no case did the sublimate of antimonous oxide show a trace of crystallization under the microscope used, nor did the arsenious oxide fail in any case to show the characteristic brilliant octahedral crystals.

The evidence that the antimonous oxide cannot appear in crystals which might be mistaken for arsenic is of course negative, but owing to the variety of forms used it must be considered to have the weight of positive evidence.

As regards the substances tested, the following may be recorded:

All arsenious compounds soluble in hydrochloric acid gave the deposit on copper immediately on heating.

Commercial "metallic" arsenic gave the deposit readily.

Freshly sublimed "metallic" arsenic (bright crystals) gave no deposit.

Arsenates gave a deposit only after several minutes boiling.

In the presence of nitric acid or chlorates no test is obtained owing to the solution of the copper.

Whenever aqua regia or potassium chlorate is necessary for solution of an arsenic compound, the solution should be evaporated to dryness with hydrochloric acid. The test can then be carried out as with arsenates.

The presence of organic matter in the arsenic solution does not affect the test, hence it can be applied directly to any organs without any previous destruction of tissue. If much arsenic is present it is best to use but a small portion of the substance, since if much arsenic is deposited on the copper, it will not adhere with firmness.

Antimony is not precipitated on the copper as rapidly as arse-

nic, and the deposit has a decidedly violet tint, very distinct from the iron gray deposit of arsenic.

The following distribution of antimony in the two cats may be added :

Acute poisoning (6 hours).	Slow poisoning (72 hours).
Stomach.—Heavy deposit and sublimate. Good test with $\frac{1}{100}$ of stomach.	Good tests.
Liver.—Not so heavy deposit as stomach. Good sublimate.	Heavy deposit and good sublimate.
Heart.—Good deposit after several hours boiling. Good sublimate.	Good deposit on ninety minutes boiling. Good sublimate.
Pancreas.—Faint deposit. No distinct sublimate.	Good deposit and sublimate.
Spleen.—Faint deposit. No distinct sublimate.	
Kidney.—Faint deposit. No distinct sublimate.	Good deposit and sublimate.
Intestine.—Good deposit and sublimate.	Good deposit and sublimate.
Muscle.—Faint deposit on two days boiling. No sublimate.	Slight violet tinge to copper. No sublimate.
Brain.—No deposit.	Marked violet tint to copper. No sublimate.
Spinal Chord.—No deposit.	

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NOTES ON THE DETERMINATION OF PHOSPHORUS IN STEEL AND CAST IRON.

BY GEORGE AUCHY.

Received August 27, 1896.

OF the many improvements made in recent years in the method of determining phosphorus in steel, that of Jones —the use of the "reductor"—is not the least. There has been, however, some difference of opinion as to the completeness of the reduction accomplished by its use. Quoting from three most recent publications on the subject: Doolittle and Eavenson consider the reduction of the molybdic acid to be to a point cor-

responding to the ratio of 89.16 iron to molybdic acid; Noyes and Royse, by special precautions, obtain a reduction completely to Mo_2O_3 (factor 85.71); and Blair and Whitfield find the ratio 88.16, a reduction to $Mo_{24}O_{37}$ only, even with the precautions of Noyes and Royse observed. Doolittle and Eavenson heat the solution before passing it through the reductor. Noyes and Royse do not. The first named chemists do not use the precautions of Noyes and Royse. It appears from a result by Prof. Noyes given in this Journal, **10**, 759, that he does not invariably get a reduction to Mo_2O_3 by his method, his result there given corroborating Blair and Whitfield's hypothesis of a reduction to $Mo_{24}O_{37}$ only.

It was thought by the writer that perhaps the reduction to Mo_2O_3 could invariably be accomplished by combining the precautions of Noyes and Royse with the practice of Doolittle and Eavenson of passing the solution through the reductor hot. The following results were obtained, using yellow phosphomolybdate precipitate dried six hours at 150° C.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0100	1.63	1.63	1.68
0.0100	1.63	1.63	1.68
0.0200	1.63	1.59	1.63
0.0300	1.63	1.63	1.68
0.0300	1.63	1.61	1.65
0.0200	1.63	1.55	1.59
0.0400	1.63	1.59	1.63
0.0500	1.63	1.62	1.67
0.0500	1.63	1.63	1.68
0.0600	1.63	1.63	1.68
0.0700	1.63	1.61	1.65
0.0700	1.63	1.60	1.64
0.1000	1.63	1.63	1.68
0.0400	1.63	1.59	1.63
0.0400	1.63	1.59	1.63
0.0200	1.63	1.58	1.62
0.0400	1.63	1.56	1.60
0.0300	1.63	1.59	1.63
0.0900	1.63	1.57	1.61
0.0400	1.63	1.60	1.64
0.0500	1.63	1.61	1.65

Passing the solution through the reductor hot does not seem to insure an invariable reduction to Mo_2O_3, and perhaps adds nothing to the effectiveness of the process. The following tests were made in the cold :

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0500	1.63	1.58	1.62
0.0400	1.63	1.59	1.63
0.0300	1.63	1.59	1.63
0.0400	1.63	1.57	1.61
0.0500	1.63	1.63	1.68

But in these last tests, and also in the first series of tests in nearly all cases where the result calculated by Noyes' factor came low, the point of the reductor had been washed off, and the sides of the flask washed down by the jet. Noyes warns against any dilution of the reduced solution before titration, but it was thought that such a slight dilution would do no harm. For a test of this the following determinations were made (cold) and without washing down :

Phosphomolybdate taken. Gram.	Phosphomolybdate present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0500	1.63	1.61	1.65
0.0900	1.63	1.60	1.64
0.0300	1.63	1.61	1.65
0.0300	1.63	1.63	1.68
0.0400	1.63	1.60	1.64
0.0400	1.63	1.63	1.68
0.0300	1.63	1.63	1.68
0.0400	1.63	1.60	1.64
0.0400	1.63	1.63	1.68
0.0500	1.63	1.62	1.67

Comparing these results with those of the preceding series it is seen that a complete avoidance of any dilution, however slight, after reduction, will bring higher results than if this precaution be neglected. But it is further seen that the observance of this precaution does not invariably assure a result agreeing with a reduction to Mo_2O_3, although it generally does so. Of the eleven results in the first series of experiments (solution passed through the reductor hot), obtained by an observance of this precaution, seven, calculated by Noyes' factor, are over 1.61 ;

and of the ten results of the last series (reduced cold), seven are 1.61 per cent. or over. On the other hand, of the thirteen results obtained by washing down the sides of the flask after reduction, ten fall short of the theoretical 1.63 per cent. by more than 0.02 per cent., calculated by Noyes' formula, and do bring 1.63 per cent. calculated by Blair's factor. The inability of Messrs. Blair and Whitfield to accomplish a reduction to Mo_2O_3 by an observance of the precautions given by Messrs. Noyes and Frohman, and also the still higher factor found by Messrs. Doolittle and Eavenson, may perhaps be due to the fact that the zinc in each case used differed in reductive power from that of the others. The writer had on one occasion zinc which when used in the reductor with all care and precautions, never gave a reduction of more than one-half; and in his opinion it is safer and more accurate to use the old Emmerton method of reduction and filtration, but with the modifications and precautions described later in this article.

The phosphomolybdate employed in the above tests, was, for part of them, made by precipitating from sodium phosphate solution; for another part of the tests, made by precipitation from pig iron solution, exactly as is done in the determination of phosphorus in pig iron. Messrs. Blair and Whitfield have shown the constancy of the composition of phosphomolybdate made under varying circumstances.

The volume of the solution passed through the reductor in each of the above experiments was 100 cc., as recommended by Blair and Whitfield. Noyes and Frohman use 200 cc., but this seems an unnecessary bulk. Fifteen cc. of sulphuric acid (2:1) was used for acidifying.

For washing 100 cc. of hot water was used containing ten cc. of sulphuric acid, (2 : 1), followed by 100 cc. cold water, and again by fifty to seventy-five cc. of cold water.

The reductor was of the form described by Blair and Whitfield,[1] except that it was considerably wider at the top than the bottom—in shape like a common tin horn. This shape holds more zinc for the given height (ten inches) of the column, and so makes the necessity of filling less frequent.

1 This Journal, 17, 74.

The reductor may be used without refilling till the column of zinc falls to five or six inches without any diminution of effectiveness. All of the results of the two preceding series, and some of the last results in the first series were obtained by the use of five to seven inches of zinc in the reductor.

It adds somewhat to the facility of the working of the apparatus to have the beaker containing the phosphorus solution above the level of the zinc in the reductor so that the connecting tube may work as a siphon. And the last washing may then conveniently be made by diminishing the force of the suction of the pump, loosening the stopper of the reductor, and allowing the water to be siphoned over and fill up the vacant space in the reductor above the zinc column.

The passage of the solution through the reductor was not preceded by the passage of dilute sulphuric acid, and in many of the tests some little air was accidentally drawn over into the reductor at the time of washing, although care was uniformly taken to allow no air to enter at the first washing.

Messrs. Noyes and Royse direct that the reductor should be rinsed with dilute sulphuric acid before using, even if it has stood but a few minutes. This is some little trouble, and to test the necessity of it, the following tests were made :

Phosphomolybdate taken. Gram.	Phosphorus taken. Per cent.	Phosphorus found. Per cent.	Reductor stood.
0.0300	1.63	1.61	one hour
0.0700	1.63	1.60	all night
0.1000	1.63	1.63	six hours
0.0300	1.63	1.63	all night
0.0300	1.63	1.63	three hours
0.0300	1.63	1.63	two days
0.0300	1.63	1.63	two days
0.0500	1.63	1.63	two days
0.0500	1.63	1.62	two days

These results seem an indication that this precaution is not absolutely necessary. But if the reductor stand nearly a week or more, the sulphuric acid will take up considerably more of the impurity of the zinc than ordinarily. Zinc, for instance, which ordinarily will require a deduction of two-tenths cc. from the amount of permanganate used in the titration, will require

a deduction of four-tenths if the reductor has stood that length of time unused.

It is necessary to remove the zinc from the reductor at intervals for cleaning, best done by stirring up in a capacious dish with hot water, adding a little sulphuric acid to clear the liquid, pouring off, washing by decantation and drying in the dish on the hot plate. But after such a treatment the zinc, after being replaced in the reductor, should be rinsed with dilute sulphuric acid before being used in analysis, as much more than the ordinary impurity of the zinc will be taken up by the sulphuric acid the first time it is used.

Perhaps a more convenient way of cleaning the zinc is to soak it (in the reductor) in water for a day (conveniently over Sunday), plugging up the ends of the reductor to retain the water. After such a treatment the reductor will go a long time without becoming clogged up with zinc oxide.

Instead of using the reductor, it is a trifle quicker and more convenient, especially when the phosphorus present is considerable as in pig iron, to use the following slight modification of the old Emmerton method of reduction and filtration.

The yellow precipitate in a seven cm. filter paper is dissolved in as little ammonia as possible, allowing to run into the eight-ounce Erlenmeyer flask in which the precipitation occurred; washed five minutes with hot water; the solution acidified with twenty-five cc. of sulphuric acid (two parts water to one part acid); a mustard spoonful of granulated zinc added (five grams), and the flask heated *gently* on the hot plate for five minutes, or until the zinc is nearly dissolved (ten minutes is required for some zinc). The flask is removed from the plate, a little dry sodium carbonate added, and when effervescence has nearly ceased the flask is corked tightly and cooled in cold water without agitating the contents any more than can be helped. The solution is then filtered from the undissolved zinc through a little cotton wool in a Hirsch funnel, smallest size, using the pump, and the flask rinsed out with cold water three times and the rinsings drawn through the cotton wool. The sides of the sixteen-ounce gas flask which receives the liquid are washed down with the jet, and the solution titrated in the flask without further dilution.

If the zinc is of the sort not dissolving very readily, thirty-five cc. of sulphuric acid should be used for acidifying the phosphorus solution instead of twenty-five cc.

The reduction is to $Mo_{12}O_{19}$. Factor of iron to molybdic acid 90.76. More correctly speaking, the reduction is to Mo_2O_3, which filtering and dilution oxidizes to $Mo_{12}O_{19}$.

It will be found upon trial that this way of reduction and filtration is somewhat easier and more rapid than the usual reductor method, as the filtration through cotton wool in a Hirsch funnel and with aid of the pump is performed as easily and quickly as merely pouring and rinsing from one vessel into another. While the zinc is dissolving in one determination, the yellow precipitate of the next determination may be filtered off.

The following results show that the reduction and filtration through cotton wool, as described, brings the molybdenum oxide to the form $Mo_{12}O_{19}$.

Considerable phosphomolybdate (four-tenths to eight-tenths gram) taken for each test.

Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.	Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.
1.63	1.63	1.63	1.63
1.63	1.63	1.63	1.62
1.63	1.62	1.63	1.63
1.63	1.63	1.63	1.63
1.63	1.63	1.63	1.62

Small amounts of phosphomolybdate taken.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.	Phosphorus present, reckoned as if from 1.8233 grams steel. Per cent. in the steel.	Phosphorus found if from 1.8233 grams steel. Per cent. in the steel.
0.2000	1.63	1.63	0.179	0.179
0.2000	1.63	1.63	0.179	0.179
0.2000	1.63	1.65	0.179	0.181
0.2000	1.63	1.63	0.179	0.179
0.1500	1.63	1.64	0.134	0.135
0.0890	1.63	1.62	0.071	0.071
0.0700	1.63	1.64	0.062	0.063
0.0700	1.62	1.63	0.062	0.062

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Factor 90.77. Per cent.	Phosphorus present, reckoned as if from 1.8233 grams steel. Per cent. in the steel.	Phosphorus found if from 1.8233 grams steel. Per cent. in the steel.
0.0600	1.63	1.64	0.054	0.054
0.0600	1.63	1.63	0.054	0.054
0.0500	1.63	1.61	0.045	0.044
0.0400	1.63	1.64	0.036	0.036
0.0300	1.63	1.64	0.027	0.027
0.0300	1.63	1.64	0.027	0.027
0.0300	1.63	1.61	0.027	0.027
0.0300	1.63	1.60	0.027	0.026
0.0400	1.63	1.62	0.036	0.036
0.0400	1.63	1.63	0.036	0.036
0.0400	1.63	1.63	0.036	0.036
0.0350	1.63	1.62	0.031	0.031
0.0380	1.63	1.63	0.034	0.034
0.0250	1.63	1.61	0.022	0.022
0.0230	1.63	1.61	0.020	0.020
0.0200	1.63	1.55	0.018	0.017
0.0200	1.63	1.51	0.018	0.017
0.0200	1.63	1.64	0.018	0.018
0.0200	1.63	1.50	0.018	0.017
0.0200	1.63	1.60	0.018	0.018
0.0200	1.62	1.55	0.018	0.017
0.0200	1.63	1.57	0.018	0.017
0.0180	1.63	1.55	0.016	0.015
0.0150	1.63	1.55	0.013	0.013
0.0150	1.63	1.55	0.013	0.013
0.0130	1.63	1.51	0.012	0.011
0.0120	1.63	1.63	0.010	0.010
0.0100	1.63	1.51	0.0089	0.008
0.0100	1.63	1.55	0.0089	0.0085
0.0100	1.63	1.46	0.0089	0.008
0.0100	1.63	1.64	0.0089	0.0089
0.0100	1.63	1.64	0.0089	0.0089

The figures in the last two columns were obtained by reckoning as though 1.8233 grams of steel had in each case been taken for analyses. In other words, these percentages in the last two columns are what they would have been had the phosphomolybdate taken been, in each case, obtained from 1.8233 grams of steel, in the regular course of analysis, for phosphorus.

It will be noticed that when the amount of phosphomolybdate

taken is very small (equivalent to 0.008 to 0.017 per cent. in steel) there is frequently some oxidation, the percentage of phosphorus in the yellow precipitate thus falling short of 1.63 by as much as 0.17 per cent. in one case. But, as will be seen by reference to the last two columns of results, this affects the result in steel but slightly.

This proneness to oxidation when very little phosphorus is present in the solution indicates that the stability of the $Mo_{12}O_{19}$ solution is greater when concentrated than when dilute. And the solution should therefore be in as small bulk as possible. Other necessary precautions are: to have a large excess of sulphuric acid present, to avoid a boiling temperature when dissolving the zinc, to cool the liquid before filtering from the undissolved zinc, to exclude air while cooling, and to filter rapidly through cotton wool in a Hirsch funnel, with aid of the pump. But where considerable phosphorus is present, as in pig irons, these precautions may be neglected, except the cooling before filtering. That is, the liquid may be cooled, after the reduction with zinc, without the addition of sodium carbonate, and with free access of air, and the filtration may be made through a seven cm. coarse paper (instead of cotton wool) by aid of the pump. The results given under the head "considerable phosphomolybdate taken for each test" were obtained in this way, air not excluded, and filtered through paper instead of cotton wool.

The advantage of making the reduction and filtration in this way in the case of pig iron is very marked when, as frequently happens, the yellow precipitate separates out when its solution in ammonia is acidified with sulphuric acid. For if the reduction be made as described, this separation may be ignored as in contact with the zinc and sulphuric acid the yellow precipitate becomes reduced and goes into solution. This is shown by the following tests, in which no ammonia was used at all. That is, the yellow phosphomolybdate precipitate was weighed directly into the reducing flasks, and thirty-five cc. of sulphuric acid (2:1) poured over, a mustard spoonful of zinc added, heated gently, etc.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Per cent.
About 0.4000	1.63	1.63
" 0.4000	1.63	1.62
" 0.4000	1.63	1.63
" 0.4000	1.63	1.62
" 0.4000	1.63	1.63

In experimenting with this process some interesting results were had. The port wine $Mo_{12}O_{19}$ solution is apparently not so stable, especially in dilute solution or with small amounts of phosphorus present, as Emmerton supposed, and certain precautions are necessary.

In the first place considerable amounts of phosphomolybdate were taken, dissolved and reduced as described, and filtered through seven cm. filter papers by aid of the pump. The results showed 1.63 per cent. phosphorus, the theoretical amount.

Several tests were then made in the same way and with the same weights of yellow precipitates, but not waiting for the solutions to cool before filtering from the undissolved zinc. Instead of the theoretical 1.63 per cent., 1.57 per cent., and 1.58 per cent. were obtained, showing the necessity of filtering cold.

Next the stability of the reduced solution was tested.

Before filtering from the undissolved zinc.	Phosphorus present. Per cent.	Phosphorus found. Per cent.
Stood two hours	1.63	1.59
" " " and poured back and forth four times	1.63	1.55
Stood one hour	1.63	1.59
" one-half hour	1.63	1.61

The flasks were not corked while standing.

Smaller weights of phosphomolybdate precipitate were then taken. The results obtained fell very much short of the theoretical, 1.63 per cent., and varied considerably. It was at first thought that the filtration by aid of the pump oxidized the solutions more than by the original Emmerton way of filtering through a large ribbed filter. But, upon making four tests and filtering in that way (Emmerton's) the results gave 1.51 per cent., 1.52 per cent., 1.46 per cent., and 1.48 per cent., respectively, instead of the theoretical, 1.63 per cent., although about

four-tenths gram yellow precipitate, was in each case taken; an amount of yellow precipitate which, when taken for the foregoing tests made by filtering through a seven cm. filter paper by aid of the pump, never failed of bringing a result equal to the theoretical. In filtering through a seven cm. filter by the pump the oxidation of the solution is therefore considerably less than the oxidation by filtering through a large ribbed filter.

An article by Blair and Whitfield[1] contains a description of an experiment made by reducing the phosphorus solution by boiling with zinc, keeping an atmosphere of hydrogen continually in the flask, and boiling till the zinc was completely dissolved; then cooling (maintaining the atmosphere of hydrogen in the flask) and titrating, the result falling considerably below the theoretical. In the case of the writer's low results just spoken of, obtained by filtering through a seven cm. filter paper by suction, the reduction had also been effected by boiling with the zinc, though not in an atmosphere of hydrogen, and not to complete solution of the zinc. Remembering the experiment of Blair and Whitfield, above quoted, it was thought that the reason for the low results in both cases lay, perhaps, in the boiling of the phosphorus solutions while being reduced, the sulphuric acid having an oxidizing effect perhaps in that case. No other reason could be offered at least for the low result in Blair and Whitfield's experiment, since, in that experiment, air had been so carefully excluded from the flask during the solution of the zinc and the cooling of the liquid. To test the matter, other determinations were made exactly as before, except that the zinc was dissolved at a gentle heat instead of by boiling. Results were much better, as will be seen in the following table. Hence the necessity for the precaution of avoiding a boiling temperature while dissolving the zinc.

Phosphorus present—1.63 per cent.

[1] This Journal, 17, 757.

Phosphomolybdate taken. Gram.	Zinc dissolved by boiling. Phosphorus found.	Zinc dissolved at a gentle heat. Phosphorus found.
0.0100	1.37	1.55
0.0200	1.37	1.50
0.0200	1.37	1.41
0.0300	1.31	1.46
0.0300	1.37	....
0.0400	1.46	1.55
0.0500	1.39	1.57
0.0600	1.28	1.60
0.0700	1.52	1.57
0.0700	1.53	....
0.0800	1.16	1.57
0.2000	1.58	1.63
0.1000	1.59	1.64

In the second column of results, the third and fourth results are considerably lower than the rest of them. But it had been noticed that in these two determinations the green color of the reduced phosphorus solution had faded to the port wine shade during the cooling of the liquid and before the filtration from the undissolved zinc, while in all the other determinations the green color had persisted till the moment of filtration. This pointed to the necessity of excluding air during the cooling of the liquid, preparatory to filtration, from the undissolved zinc, and the precaution was accordingly adopted of corking the flask while cooling, first adding a little sodium carbonate to fill the flask with carbon dioxide. Results by this procedure follow.

As the flask is already filled with hydrogen gas from the solution of the zinc, and vapor from the heating of the liquid, it is perhaps unnecessary to add the sodium carbonate at the end of the reduction. In that case the flask should be corked with a one-hole cork with drawn-out glass jet, during the solution of the zinc; and the jet closed when the reduction is completed.

It was thought that results agreeing more closely and uniformly with the theoretical might be obtained by filtering through cotton wool instead of paper, as the filtration can be considerably more quickly accomplished in that way, even when much suction is used in the latter way. Results showed this to be the case, and are also given below in comparison with results by filtering through paper.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Filtration through paper. Phosphorus found. Per cent.	Through cotton wool. Phosphorus found. Per cent.
0.0100	1.63	1.41	1.55
0.0100	1.63	....	1.64
0.0100	1.63	....	1.46
0.0100	1.63	....	1.64
0.0100	1.63	....	1.46
0.0200	1.63	1.46	1.50
0.0200	1.63	1.48	1.60
0.0200	1.63	1.48	1.64
0.0200	1.63	....	1.63
0.0200	1.63	....	1.55
0.0200	1.63	....	1.57
0.0300	1.63	1.58	1.64
0.0300	1.63	1.57	1.63
0.0300	1.63	....	1.64
0.0300	1.63	....	1.61
0.0400	1.63	1.55	1.64
0.0400	1.63	....	1.62
0.0500	1.63	1.57	1.61
0.0600	1.63	1.57	1.64
0.0600	1.63	1.60	1.63
0.0700	1.63	1.60	1.63
0.0800	1.63	1.62	....

From these results it is seen that cotton wool is much better for use in filtering from the undissolved zinc than paper. Very little pressure is required with the former and very little cotton wool is required. A small Hirsch funnel is necessary. But the cotton wool should not be pressed down with the finger after it is wet, but sucked down by the pump. In the above experiments the filtrations through paper were also accomplished by a Hirsch funnel, smallest size. (Paper size, seven cm.)

Using cotton wool, no oxidation of the port wine, $Mo_{12}O_{19}$, solution need be feared where the amount of phosphorus present is that which in a sample of steel (one and eight-tenths grams) would be equivalent to 0.020 per cent. or over; while with percentages under 0.020 the oxidation is never greater than will make a difference of 0.001 per cent. in the result.

All the foregoing experiments were made with the use of zinc, requiring about ten minutes for solution. This supply becom-

ing exhausted, new zinc was procured which happened to dissolve much more freely in acid, and experiments were therefore made as before but using only fifteen cc. of sulphuric acid for solution of the zinc instead of thirty-five cc. as before with the first lot of zinc. Results were noticeably lower, pointing to the inference that a large excess of sulphuric acid present is necessary as favoring the stability of the $Mo_{12}O_{19}$ port wine solution. Other determinations were then made, using twenty-five cc. of acid.

Phosphorus present, 1.63 per cent.

Phosphomolybdate taken. Gram.	Fifteen cc. sulphuric acid. Phosphorus found. Per cent.	Twenty-five cc. sulphuric acid. Phosphorus found. Per cent.
0.0400	1.63	....
0.0380	1.63	....
0.0350	1.62	....
0.0320	1.51	....
0.0300	1.55	1.60
0.0280	1.53	....
0.0250	1.50	1.61
0.0230	1.50	....
0.0230	1.55	1.61
0.0200	1.48	1.51
0.0200	1.55	1.55
0.0180	1.47	1.55
0.0180	1.48	....
0.0150	1.46	1.55
0.0150	....	1.55
0.0160	....	1.54
0.0140	....	1.56
0.0130	1.40	1.51
0.0100	1.40	1.51

This shows the necessity for the precaution of using plenty of sulphuric acid for solution of the zinc.

As before pointed out, results by the foregoing procedure, using all precautions, never fail of the theoretical, 1.63 per cent., or a reasonable approximation thereto, except when the amount of phosphomolybdate taken is only 0.0200 gram (equivalent to 0.018 per cent. in all steel determinations) or less, and the error in that case in a steel never amounts to more than 0.001 per cent. with about two grams of steel taken for analysis; and

the writer therefore, on the score of accuracy, prefers this method to the reductor method.

A convenience in phosphorus determinations is a Mohr burette for the sulphuric acid, attached to the sulphuric acid bottle by tubing reaching just to the zero mark of the burette according to the well known plan. The bottle should stand high, and the tubing be wide so that too much lung power will not be required to fill the burette. The delivery tube of the burette should also be of a good width, so that the acid may run quickly into the phosphorus solutions. The apparatus is also convenient for Elliott sulphur determinations, using sulphuric acid for acidifying the caustic soda sulphur solution instead of hydrochloric acid.

There is some difference of opinion among chemists as to the advisability of using sugar for reducing the manganese precipitate formed by the addition of permanganate to the boiling nitric acid solution of the steel. Sugar was originally recommended by Dr. Drown, but Mr. Clemens Jones, obtaining varying results which he attributed to its use, substituted ferrous sulphate with very satisfactory results. Dr. Dudley also states that in using sugar a different result is obtained than when ferrous sulphate is used. On the other hand, Handy and others have claimed that sugar has no harmful effect. The following tests were made by the writer:

No.	Using ferrous sulphate. Phosphorus. Per cent.	Using sugar. Phosphorus. Per cent.
Steel 618	0.017	0.018
" 620	0.018	0.018
Gray pig iron	0.719	0.720
Test bar	0.016	0.016
Steel 684	0.049	0.049
Phosphate solution	0.123	0.121

These results were considered sufficient evidence that sugar does not interfere with the precipitation of the phosphorus. Its use is more advantageous in several respects: it is cheaper than ferrous sulphate; less of it is required; it may be added to the boiling solution without fear of the solution boiling over; and it never contains phosphorus.

The merest pinch of sugar will suffice to reduce a very abundant precipitate of manganese peroxide if the boiling be continued for some time after its addition to the liquid.

For the filtration of the yellow phosphomolybdate precipitate with the aid of the pump, it is the writer's experience that nothing succeeds so well as two seven cm. Schleicher & Schüll No. 579 filter papers, folded and placed in the funnel together. The filtration may be made very rapidly, yet without any of the precipitate going through the paper.

After the solution of the yellow precipitate on the filter paper in ammonia and washing, the same filter may be used (without removal from the funnel) for another phosphomolybdate filtration, and so on for a number of consecutive determinations.

No. 579 is a very loose and porous paper. No. 589 *black ribbon* also serves.

SOME NEW COMPOUNDS OF THALLIUM.

BY L. M. DENNIS AND MARTHA DOAN, with Crystallographic Notes, by A. C. Gill.

Received September 4, 1896.

THALLOUS TRINITRIDE, TlN_3.

WHEN a concentrated solution of potassium trinitride containing a little free hydronitric acid is added to a solution of thallous sulphate, a white, finely crystalline precipitate is formed. This compound is soluble in hot water, and when recrystallized from a hot aqueous solution, it separates in orthorhombic needles of a light straw color.

The thallium in this salt was determined volumetrically by means of a standard solution of potassium permanganate, according to the method of Willm.[1]

In the case of the hydronitric acid, a volumetric method also was first attempted. A weighed portion of the salt was dissolved in water and placed in a Hempel distilling bulb, which was connected by fused joints to a condenser. A separatory funnel was inserted in the neck of the distilling bulb. The hydronitric acid was set free by the addition of an excess of dilute sulphuric acid and was distilled into an Erlenmeyer flask containing a known amount of ammonia, the excess of ammonia being then deter-

[1] *Ann. chim. phys.*, (4), 5, 79.

mined by titration. It was at first difficult to drive over all of the hydronitric acid, the results being uniformly low with one exception, and in that case the distillate gave a reaction for sulphuric acid. The results continued poor in spite of various modifications which were tried, so that finally recourse was had to the gravimetric method, this not having been used before because of the explosive character of the silver trinitride. A weighed portion of the salt was dissolved in water and precipitated with a neutral silver nitrate solution. The silver trinitride was thoroughly washed by decantation with cold water, the washings being passed through a Schleicher and Schüll hardened filter No. 575. The precipitate was then transferred to the paper, the point of the filter carefully perforated and the precipitate washed through into a weighed porcelain crucible. Hydrochloric acid was then added to the contents of the crucible and the whole evaporated to dryness. By this treatment the silver trinitride is decomposed and the hydronitric acid expelled, together with the excess of hydrochloric acid. The silver chloride remaining in the crucible was then weighed, and from its weight the amount of nitrogen in the salt was computed. The results were:

		Calculated for TlN_3.	Found.
Thallium	204.18	82.9	82.87
Nitrogen	42.09	17.1	17.2
	246.27	100.0	100.07

The prism angle could be measured on the goniometer, but the end faces were too small to give good reflections. The trace of the macrodome on the prism face was measured repeatedly on the microscope stage, giving an angle of 51° 30′ with the vertical edge. The prism angle, $110 : \overline{1}10 = 79° 50'$. Hence the axial ratio:

$$\breve{a} : \bar{b} : \acute{c} = 0.8366 : 1 : 1.2407.$$

The crystals were composed of many fine needles, sometimes twinned on the prism face (110), but more frequently in parallel growth. The double refraction was strong, and the plane of the optical axes is at right angles to the long direction of the needles, *i. e.*, = 0.001.

Thallous trinitride is somewhat soluble in cold water and is easily soluble in hot water. It is not explosive, resembling in this particular the trinitrides of potassium and sodium. It melts without decomposition when heated in an atmosphere of carbon dioxide. Its melting point was determined by placing some of the crystals in a small glass tube in the top of which was inserted a cork with two holes. Carbon dioxide was passed into the tube through one of these openings, and a small exit tube was inserted in the other. The tube was heated by immersing it in a bath containing an easily fusible alloy, and the temperature was measured with a carbon dioxide filled thermometer corrected by the Physikalisch-Technische Reichsanstalt of Charlottenburg. The corrected temperature at which the crystals melted was 334°.

When exposed to the sunlight, the crystals of thallous trinitride assume a dark brown appearance, which is probably due to the formation of thallous oxide. This change must be very superficial, however, as no change in weight could be detected in a sample which had been in a southern exposure for two months.

When heated in a current of dry nitrogen, thallous trinitride was easily reduced. The hydrogen on leaving the combustion tube, in which the boat containing the thallous trinitride was placed, was passed through two bulbs containing water. The aqueous solution thus obtained had a very distinct odor of ammonia, turned turmeric paper brown, and when neutralized with hydrochloric acid and allowed to spontaneously evaporate over sulphuric acid and caustic potash, it yielded crystals which under the microscope were identical with those of ammonium chloride. The ammonia found in two of the reductions in hydrogen was titrated with standard acetic acid, this acid being used in order that only the free ammonia might be neutralized and any ammonia which might be present combined with hydronitric acid would remain as such.[1]

In one case 29.83 per cent. of the nitrogen in the trinitride acid was converted into ammonia; in the other 27.37 per cent. of the nitrogen was thus changed.

[1] HN_3 is somewhat stronger than glacial acetic acid. *J. prakt. Chem.*, (2), 43, 207.

Hydronitric acid was tested for in the aqueous solution by addition of silver nitrate to the solution in which the ammonia had been neutralized, and in each case only a trace was found. It was thought that perhaps the formation of the acid might be due to the presence of a small amount of moisture in the hydrogen, so a reduction was made with hydrogen which had been passed through a piece of moist cotton. In this case 21.55 per cent. of the nitrogen was converted into ammonia, and as before only a small amount of hydronitric acid was formed.

The highest results for the nitrogen converted into ammonia approximate one-third of the total nitrogen present, and inasmuch as only a trace of the nitrogen is found to exist in the form of hydronitric acid, it is possible that the molecule of the acid breaks down thus:[1]

$$\left.\begin{matrix} N \\ \| \\ N \end{matrix}\right\rangle N-H + \begin{matrix} H \\ H \end{matrix} = N_2 + N \begin{matrix} /H \\ -H \\ \backslash H \end{matrix}.$$

THALLOUS THALLIC TRINITRIDE, $TlN_3.TlN_9$.

It was thought that thallic trinitride might be obtained by the solution of freshly precipitated thallic hydroxide in hydronitric acid. The hydroxide when treated with hydronitric acid and warmed, dissolved to a clear straw-colored solution, but when the solution was allowed to stand at ordinary temperature, hydronitric acid escaped and thallic hydroxide was precipitated. Concentration of the solution was tried by placing it in a freezing mixture and removing the water as ice. From the liquid thus concentrated, bright yellow crystals separated, yet so much of the salt solution was occluded in the ice that this method proved wasteful. The best yield of crystals was obtained by dissolving the thallic hydroxide in a one and six-tenths per cent. solution of hydronitric acid and allowing the solution to stand at a temperature of about zero in a Hempel desiccator which was exhausted by means of a common suction pump. Glistening, yellow, needle-shaped crystals appeared. They were removed in five fractions, which under the microscope seemed to be alike and homogeneous.

[1] The further investigation of this reaction is now being carried on in this laboratory. D.

These sharply outlined crystals verged toward a brown color in the larger specimens. On the stage of a microscope they showed either parallel extinction, or an extinction of 42°. That is, the long direction of the crystals varied in different individuals. The crystals were probably triclinic, though there is a possibility that they furnished a case of flattening, parallel to the face of the orthorhombic pyramid. An optical axis emerged obliquely from the tabular face, showing that it was not really, as would otherwise appear, the pinacoid of an orthorhombic crystal. The plain angles were 132°, 132° and 96°. The double refraction was not very strong.

The thallium was determined by dissolving some of the crystals in dilute hydrochloric acid, reducing the thallium to the thallous condition by sulphurous acid, driving off the excess of the latter acid by heating the solution and then titrating with potassium permanganate. The nitrogen could not be determined by the method used for thallous trinitride, because the salt could not be dissolved either in water or dilute acids without evolution of hydronitric acid. For this reason the absolute method was used. We had already found that the salt was highly explosive, but the behavior of the thallous trinitride, when heated in an atmosphere of carbon dioxide, led us to attempt the decomposition of a small portion of this substance in a similar manner. A few milligrams were, accordingly, spread over the bottom of a long porcelain boat, which was placed in a combustion tube containing granular copper oxide. The tube was connected at one end to a carbon dioxide generator, and at the other to a Schiff nitrometer. The exit end of the tube was heated to redness and the heat was then run back very carefully toward the boat. Gradual decomposition of the compound, however, was not attained, for when the temperature in the neighborhood of the boat had risen but slightly, the salt exploded violently, shattering the boat and tube. Another portion of the hydronitride was then mixed with granular copper oxide and heated as before. The decomposition in this case was quiet and gradual. The nitrogen in the nitrometer amounted to 27.32 per cent. of the salt taken. It seemed possible, however, that in mixing the hydronitride with the coarse copper oxide, some of the salt

might have been decomposed by the friction, and that consequently the above per cent. of nitrogen might be too low. To ascertain if this were true, a fresh portion of copper oxide was ground very fine and was then carefully mixed with a small portion of the salt. In this way higher results were obtained.

The analysis gave:

		Calculated for TlN_6.	Found.
Thallium	204.18	70.81	70.70
Nitrogen	84.18	29.19	29.3
	288.36	100.00	100.00

If this were a simple compound, the thallium would seem to be in the bivalent condition, but as this is at variance with the usual behavior of the element, it seemed more probable that the compound is a double salt containing thallium in both the thallous and thallic condition. This supposition was confirmed by the behavior of the crystals when treated with hot water. Brown thallic hydroxide separated, and upon filtering this off and adding potassium iodide to the filtrate, a precipitate of thallous iodide resulted. Instead, however, of finding only fifty per cent. of thallium in the thallous condition, as would be required by the formula $TlN_3.TlN_9$, there was obtained 63.7 per cent. This excess of thallous thallium is doubtless due to the reduction of some of the thallic hydroxide by the hydronitric acid set free when the salt is treated with hot water.

Thallous-thallic trinitride is highly explosive, the decomposition being accomplished by a sharp report and a vivid flash of green light. The explosion can be brought about by heat, percussion or even gentle friction.

THALLOUS TELLURATE, Tl_2TeO_4.

In 1878 F. W. Clarke prepared what he supposed to be thallous tellurate by precipitating a thallous nitrate solution with ammonium tellurate.[1] The amount obtained was so small that no analysis was made.

To avoid the presence of other salts in the solution, we used a solution of thallous hydroxide and precipitated that by adding a

[1] *Ber. d. chem. Ges.*, 11, 1507.

solution of pure telluric acid. The white, flocculent precipitate which formed was washed with cold water, transferred to a filter and dried over calcium chloride.

In the analysis of this substance, the thallium was determined by the method above described. Considerable difficulty was encountered in the determination of the tellurium, the presence of thallium making it impossible to use either the potassium permanganate titration or the method recently described by Gooch.[1] The thallous tellurate was soluble in water, but the amount of water required for its solution was so great that the telluric acid could be precipitated by neither lead nor barium solutions. For these reasons the method of Kastner[2] was used, the tellurium being precipitated in alkaline solution by means of grape sugar. As some thallium separated with the tellurium, the precipitate was treated with nitric acid and the acid then driven off by evaporation. The thallous nitrate was removed by washing the residue with water and the tellurous oxide was filtered in a Gooch crucible, dried and weighed. The results were :

		Calculated for Tl_2TeO_4.	Found.
Thallium	408.39	68.13	68.17
Tellurium	127.00	21.19	21.19
Oxygen	64.00	10.68	(diff.) 10.64
	599.36	100.00	100.00

Thallous tellurate is slightly soluble in water, and it was hoped that there might be obtained from the aqueous solution crystals sufficiently well defined to admit of a comparison of them with those of thallous sulphate and thallous selenate. Unfortunately, however, it was found impossible, in spite of many and varied attempts, to obtain anything but a white amorphous powder. Even when a solution saturated at 40° was allowed to slowly cool to 15° through a period of eight days, no crystals resulted.

THALLOUS CYANPLATINITE, $Tl_2Pt(CN)_4$.

Carstanjen prepared what he reported to be thallous cyanplat-

[1] *Ztschr. anorg. Chem.*, 7, 132.
[2] *Ztschr. anal. Chem.*, 14, 142.

inite by neutralizing cyanplatinous acid with thallous carbonate.[1] The compound was given the formula TlCN.PtCN, although no analytical results were given.

The cyanplatinous acid used by us in the preparation of the thallium cyanplatinite was obtained according to the method of Schafarik.[2] It was neutralized by thallous hydroxide, which was prepared by precipitating a thallous sulphate solution with the calculated amount of baryta water. The crystals separated out in the form of thin plates.

A determination of the thallium and cyanogen gave the following results:

		Calculated for $Tl_2Pt(CN)_4$.	Observed.
Thallium	408.36	57.73	57.7
Platinum	195.00	27.56	...
Cyanogen	104.12	14.71	14.5
	707.48	100.00	

The crystals are nearly colorless plates, usually very thin and occurring irregularly grown together on the flat sides. The crystal system was not positively determinable from the material at hand, but is probably triclinic, possibly monoclinic with crossed dispersion. In converged polarized light, a bisectrix is seen nearly or quite normal to the large face of the plates, and the dispersion of the planes of the optic axes is remarkably strong, so that the crystals simply change color without becoming dark on rotation between crossed Nicols. The double refraction is high. The plates are bounded by crystal faces, giving them a six-sided outline, but on the material used no goniometric measurements could be made.

CORNELL UNIVERSITY,
AUGUST 1896.

1 *J. prakt. Chem.*, 102, 144.
2 *Ibid.*, 66, 401.

NOTES ON THE ESTIMATION OF CAFFEIN.

By W. A. Puckner.

Received September 2, 1896.

SOME time ago Gomberg published a method for the estimation of caffein, by means of Wagner's reagent,[1] wherein appear certain statements from which is to be inferred the superiority of this method over such where the caffein is shaken out of an aqueous solution by means of chloroform, and which, if true, would show that most methods now in use, give low results since but an imperfect separation of caffein is attained. Thus Spencer[2] is said to have demonstrated the difficulty with which the alkaloid is abstracted from watery solutions, he directing that at *least* seven portions of chloroform be used for this purpose, but offering no proof of the necessity for this departure from the usual direction of shaking out the liquid with three or four portions of the solvent. Spencer is at variance with Allen,[3] who investigated this matter and found that from a solution, slightly acidulated with sulphuric acid, one treatment with chloroform removed seventy to eighty-five per cent. of the amount present, while four usually effected complete extraction, especially if toward the end the solution is rendered faintly alkaline.

This agrees well with the results of my own experiments, where anhydrous caffein, in quantities from one-tenth to four-tenths gram, dissolved in fifty cc. one per cent. sulphuric acid, was shaken successively with twenty-five, ten and ten cc. chloroform, the united chloroform solution evaporated at a gentle heat and the residue dried over sulphuric acid to constant weight. In each case the solution was shaken with a further quantity of ten cc. chloroform and the weight of the caffein so extracted ascertained as before.

Caffein taken. Gram.	Residue from first, second and third extraction. Gram.	Residue from fourth extraction. Gram.	Total per cent. recovered.
0.1285	0.1277	0.0004	99.69
0.1852	0.1820	0.0026	99.67
0.1988	0.1980	0.0002	99.69
0.2011	0.1977	0.0025	99.55
0.2559	0.2552	0.0005	99.92
0.4416	0.4355	0.0043	99.58

1 This Journal, 18, 331.
2 *J. Anal. Chem.*, 4, 390.
3 Com. Org. Anal., 3, Part II, 485.

This shows that the extraction of caffein from an aqueous solution presents no difficulties since, even when the solution is quite acid, practically the entire amount is obtained when four portions of chloroform are used; while, even if the fourth be omitted the results will be sufficiently correct for most purposes.

In the article referred to we are also told, although it is usually stated caffein may be shaken out of an acid solution, since its salts are broken up by water, that this is but relatively true; as a proof thereof the following is offered:

"1.0085 grams of caffein were dissolved in sixty cc. of sulphuric acid (1.10), and this solution was repeatedly shaken with chloroform, twenty-five cc. at a time:

Ten consecutive portions of chloroform	gave a total of	0.3514	gram	caffein.
Three additional " " "	made " "	0.4859	"	"
Three more " " " "	" " "	0.5034	"	" "

Since the degree of dissociation of caffein salts is inversely proportional to the acid strength of the solution, it is to be expected that it will be extremely difficult to shake out the alkaloid from a solution containing so great a quantity of free acid; but while at times it may be advantageous to extract caffein from a solution having an acid reaction, in no instance would there seem need of a sufficient amount to render the method inapplicable; further, according to Knox and Prescott[1] Gomberg's method becomes uncertain under similar conditions.

In the experiments just quoted ten extractions with chloroform yielded but 34.85 per cent. of the total caffein, or on an average each treatment removed only 3.485 per cent., while the three subsequent treatments removed an additional 13.33 per cent. of the whole, or 4.44 per cent. for each extraction, *i. e.*, although the total substance in solution had been decreased by more than one third the average amount given up to chloroform increased in the 11th, 12th and 13th treatment; while in the 14th, 15th and 16th but 1.735 per cent., or on an average of 0.578 per cent. for each shaking was obtained.

Although the writer had never attempted a caffein determination under the conditions mentioned, he was, from theoretical considerations, inclined to question the figures given, and accordingly made the following experiments.

[1] Proceedings Am. Pharm. Ass., *1896*.

1.0137 gram caffein, rendered anhydrous by keeping in a desiccator over sulphuric acid until its weight remained constant, was dissolved in sixty cc. ten per cent. sulphuric acid and shaken successively with nine portions of chloroform, twenty-five cc. each ; the chloroform solutions evaporated at a gentle heat and the residue dried over sulphuric acid to constant weight.

1st portion of twenty-five cc. yielded a residue of	0.5525	gram.
2nd " " " " " " " "	0.2514	"
3rd " " " " " " " "	0.1155	"
4th " " " " " " " "	0.0535	"
5th " " " " " " " "	0.0237	"
6th " " " " " " " "	0.0114	"
7th " " " " " " " "	0.0058	"
8th " " " " " " " "	0.0029	"
9th " " " " " " " "	0.0015	"
	1.0182[1]	"

In the second experiment 1.0001 gram anhydrous caffein in sixty cc. ten per cent. sulphuric acid, extracted as before, with chloroform in proportions of twenty-five cc. each :

1st, 2d and 3rd portions gave a total residue of	0.9086	gram.
4th, 5th and 6th " " " " " "	0.0854	"
7th, 8th and 9th " " " " " "	0.0134	"
	1.0074[1]	"

The sulphuric acid used in Gomberg's experiments was designated as "(1:10)" by which it is presumed an acid containing ten per cent. by weight of sulphuric acid was meant ; since, however, it was possible that sulphuric acid 1:10 *by volume* was the strength of the acid used, a determination was made with an acid with such concentration, *i. e.*, ten cc. concentrated sulphuric acid mixed with water enough to make when cold, 100 cc. In sixty cc. of this were dissolved 0.9790 gram caffein and extracted with chloroform in portions of twenty-five cc. each as before.

1st, 2nd and 3rd portion yielded a total residue of	0.6484	gram.
4th, 5th and 6th " " " " " "	0.2222	"
7th, 8th and 9th " " " " " "	0.0756	"
10th, 11th, 12th, 13th, 14th, 15th and 16th " "	0.0379	"
	0.9841[1]	"

[1] No explanation is offered to account for the plus error in the above. Contamination with sulphuric acid was suspected, but disproved.

As was to be expected, this confirms in a general way, the statement relative the difficulty with which caffein is shaken out of solutions containing a large proportion of sulphuric acid ; in no way, however, does it agree with the data given by Gomberg, who by ten successive treatments with chloroform removed only 34.85 per cent., while my figures show that when a ten per cent. sulphuric acid was used, with but three extractions, fully ninety per cent. was recovered, and even with a still stronger acid (1 + 9 by volume), three portions of chloroform removed about sixty-five per cent.

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CONTRIBUTION TO THE KNOWLEDGE OF THE RUTHENOCYANIDES.

BY JAS. LEWIS HOWE.

Received August 27, 1896.

POTASSIUM ruthenocyanide was described by Claus, in 1854, in his "Beiträge zur Chemie der Platinmetalle." The salt was formed by fusing ammonium ruthenitrosochloride[1] (tetrachloride of Claus) with potassium cyanide. The attempt was also made to form it by fusing potassium ferrocyanide with ruthenium, but it was found impossible to separate the ferrocyanide and ruthenocyanide. It is probable that some of Claus' experiments were carried out with a ruthenocyanide contaminated with ferrocyanide, from the fact that he describes copper ruthenocyanide as brown, whereas, when free from the ferrocyanide, it is pale green. Potassium ruthenocyanide in reactions and crystallization resembles very closely the ferrocyanide, except that when pure it is white. Its crystallography as well as that of the isomorphous ferrocyanide and osmocyanide are described by A. Dufet.[2]

Preparation of potassium ruthenocyanide for the purpose of carrying out experiments upon it not yet completed, gave occasion to the work recorded in this paper.

In the Claus method of preparation, a large proportion of the ammonium ruthenitrosochloride is decomposed with separation of metallic ruthenium, and while a part of the ruthenocya-

[1] Joly : *Compt. rend.*, 108, 854, *1889* ; Howe : *J. Am. Chem. Soc.*, 16, 388, *1894*.

[2] *Compt. rend.*, (*1895*), 120, 377.

nide formed crystallizes out from a solution of the melt, in large square pseudorhombic plates, much is left in the solution and cannot be directly separated from the potassium cyanide and other salts present. Attempts were therefore made to use other methods of formation with the following results:

1. Potassium rutheninitrosochloride, K_2RuCl_5NO, fused with potassium cyanide, gave rather better results in ruthenocyanide, there being rather less decomposition than was the case with the ammonium salt.

2. Ruthenium trichloride, $RuCl_3$, fused with potassium cyanide gave a fair product of ruthenocyanide.

3. Metallic ruthenium, fused with potassium cyanide, was slightly acted upon, giving a trace of ruthenocyanide.

4. Metallic ruthenium, fused with potassium cyanide and a little potassium hydroxide, gave rather stronger reaction than case 3, but the amount of ruthenocyanide formed was very small.

5. The melt formed by fusion of ruthenium in potassium hydroxide and nitrate, containing potassium ruthenate, K_2RuO_4, was dissolved in water and boiled with potassium cyanide. The deep orange-red solution was quickly decolorized and the ruthenium was converted into ruthenocyanide with little loss. A considerable proportion could be obtained in the usual square crystals. This process could, by modification, probably be made the most satisfactory method of forming the ruthenocyanide, presenting one decided advantage that metallic ruthenium, or oxides, can be used, thus avoiding the necessity of preparing the nitrosochloride or chloride.

6. Ruthenium trichloride was boiled with a strong solution of potassium cyanide. The ruthenocyanide, crystallizing in the usual square form, was obtained, but very much contaminated with a greenish by-product not yet investigated, probably analogous to Prussian blue.

7. Potassium rutheninitrosochloride was boiled with a strong solution of potassium cyanide. The solution was slowly decolorized, considerable of the greenish by-product being formed. From this solution there crystallized thick straw-colored hexago-

nal plates, which will be considered further on. The quantity of the product is not satisfactory.

8. The Weselsky method[1] of forming double cyanides was tried. Hydrocyanic acid was led into a solution of the nitrosochloride, in which barium carbonate was suspended, until effervescence ceased. The solution gave no reaction for ruthenocyanide. Its color had changed to the brown-yellow of the trichloride, but gave no reaction for this with potassium thiocyanate, or with ammonia and sodium thiosulphate. On warming, the solution gelatinized to a firm hydrogel, insoluble in hot aqua regia, but soluble in boiling potassium hydroxide. This last solution was unchanged on acidification with hydrochloric acid, and gave the potassium ferrocyanide reaction for nitrosochloride, but no reaction for trichloride. The dried jelly was easily explosive on heating. It presents an interesting analogy to Jackson's[2] hydrogel of cobaltocyanide and is being further studied.

9. The Weselsky method was also applied to ruthenium trichloride. The merest trace of ruthenocyanide was formed, and the solution, little changed in color, no longer gave reactions for the trichloride.

10. The nitrosohydroxide of Joly, formed by the precipitation of the chloride by potassium carbonate, is easily soluble in potassium cyanide and converted into ruthenocyanide by prolonged boiling.

The following reactions of ruthenocyanide may be noted:

No precipitates are formed with the caustic alkaline earths, their ruthenocyanides being soluble in water.

Lead acetate gives a fine white precipitate, soluble in nitric acid.

Silver nitrate gives a white curdy precipitate, insoluble in both ammonia and in nitric acid.

Ferric chloride gives a rich purple precipitate, closely resembling Prussian blue in its chemical properties. In pure water it is soluble, but is precipitated from this solution by salts or alcohol. It forms a very beautiful and intense dye, adhering with

1 Weselsky, Sitzber. Akad. Wien., **60**, ii. (*1870*), 261; *Ber. d. chem. Ges.*, **2**, 588, *1869*.
2 Jackson: *Ber. d. chem. Ges.*, **29**, 1020, *1896*.

great persistence to cotton fiber, on which it has been precipitated. It is decomposed very readily by alkalies with precipitation of ferric hydroxide, re-forming, however, on the addition of acids, unaffected by dilute acids, but permanently decomposed by strong acids. It is a most delicate reaction for the detection of ruthenocyanide.

Ferrous sulphate gives a pale blue precipitate, which gradually changes to the purple above mentioned, and instantly if bromine water is added.

Copper sulphate gives a very pale green flocculent precipitate (not brown as given by Claus).

With salts of the following metals precipitates are formed insoluble in hydrochloric acid: Cadmium, white (soluble in hot acid); zinc, white; tin (both stannous and stannic), white; mercury, white; bismuth, white (insoluble in nitric acid); nickel, dirty green (changing to blue with hydrochloric acid); cobalt, pale red; platinum, yellow-green; manganese gives a white precipitate soluble in hydrochloric acid. With gold there is no immediate precipitate, but a gradual darkening and separation of a dark precipitate, the solution becoming green.

Bromine water changes the solution to a dark red, which does not give the trivalent ruthenium reaction. Iodine also seems to alter the solution.

No reaction with hydrogen sulphide, ammonium sulphide, or thioacetic acid.

Nitric acid has no effect in the cold, but when heated slightly reddens the solutions. It then shows no signs of a reaction analogous to that of the nitroprussides.

It is acted on by potassium nitrite with sulphuric acid, and when neutralized gives a fugitive rose red with ammonium sulphide.

It gives no apparent reaction with ruthenium trichloride or nitrosochloride.

Two methods of purification, applicable to such portions of the ruthenocyanides as cannot be separated by crystallization, may be used. The most satisfactory is the precipitation in dilute solution by lead acetate and thorough washing with hot water to remove any lead chloride present. Suspension of the lead

ruthenocyanide (carbonate, cyanide, etc.) in much water and decomposition with dilute sulphuric acid. Filtration and addition of baryta water till nearly neutral and then of barium carbonate in excess; warming, filtration, and evaporation to crystallization of the barium ruthenocyanide from which other ruthenocyanides may be formed by double decomposition.

The other method of purification which is applicable especially to all residues, is precipitation with ferric chloride in slightly acid solution, washing with acidified water, as far as possible (the purple begins to dissolve as the salts are washed out) and decomposing with baryta water. This method, while very useful for recovery of residue, does not give so pure a product as the first method.

The hexagonal crystals described above, in process 7, presented points of interest, in that it seemed not impossible that they contained the nitroso group of the nitrosochloride from which they were formed. When dissolved in water they showed every reaction of the ordinary square crystals of the ruthenocyanide, but they could not be converted into the square form by recrystallization nor could their yellowish tint be removed. The crystals are anhydrous while the white crystals contain three molecules of water of crystallization. On heating they explode with considerable violence while the square crystals decompose very gently. On recrystallization they show prismatic forms, with many twins resembling staurolite crosses, and others resembling aragonite twins. Though perfectly hexagonal in form, they do not seem to belong to the hexagonal system. After conversion into the lead, hydrogen, barium, and back into the potassium salt by the first method of purification described, and further precipitation of this potassium salt by alcohol and recrystallization from water, crystals were obtained which were square, white, and in every respect, crystallographically as well as chemically, resembled the ordinary potassium ruthenocyanide. This was verified by analysis of the barium salt and partial analysis of the potassium salt.

It is evident that the hexagonal crystals are not a nitrosocyanide, and it seems possible that the form may be conditioned by

some trace of impurity. They are being further studied at present.

ANALYSIS OF POTASSIUM AND BARIUM RUTHENOCYANIDES.

Potassium ruthenocyanide, $K_4Ru(CN)_6,3H_2O$, formed by boiling a solution of potassium rutheninitrosochloride with potassium cyanide; purified by conversion through lead, hydrogen, and barium salts.

		Per cent.
I.	Loss of water in four days standing over sulphuric acid	10.84
II.	" " " at 120°	10.90
III.	" " " in 30 hours standing over sulphuric acid	11.25
	Theory for $K_4Ru(CN)_6,3H_2O$. $3H_2O$ =	11.53

The crystals, especially when small, are so efflorescent that it is difficult to obtain uneffloresced salt for analysis, and the following are calculated for the dehydrated salt.

	Theory for $K_4Ru(CN)_6$.	Found. I.	II.	III.
Potassium	37.76	37.22	38.32	37.28
Ruthenium	24.53	23.90	24.22	24.44

This corresponds to the potassium ruthenocyanide described by Claus.

Barium ruthenocyanide, $Ba_2Ru(CN)_6,6H_2O$, (new) formed from the ordinary form of the potassium salt.

Pale straw-colored, diamond-shaped (up to one-half cm. long) monoclinic crystals, or larger crystal rosettes, slightly soluble in cold, more easily in hot water, slowly lose water of crystallization over sulphuric acid, lose five and a half molecules of water at 100° but retain one-half molecule to nearly 200°, thus resembling barium ferrocyanide. The barium ruthenocyanide from the hexagonal form of the potassium salt was similar, but was not obtained in well enough defined crystals to identify positively with the preceding, but analysis shows the constitution to be the same.

The method of analysis was the following: The salt was heated in a platinum boat (in two cases porcelain was used and attacked, so that the ruthenium was contaminated by silica—Analyses I and V) in an oxygen current, and the carbon

dioxide evolved collected in an absorption apparatus. The proportion given off was variable, but usually a little more than five atoms. The boat was then heated in a hydrogen current, to reduce the oxide of ruthenium formed. The boat was then placed in a carbon dioxide apparatus and treated with hydrochloric acid and the remainder of the carbon dioxide collected. The barium chloride was then filtered off from the ruthenium and determined as sulphate; the ruthenium, after burning the filter paper and heating in a hydrogen current in a porcelain boat, was estimated as the metal. It was not found possible to arrive at any agreement in different analyses as to the loss on heating the barium salt in air, or oxygen, or subsequently in hydrogen. While most of the carbon of the cyanogen is burned to carbon dioxide, a part remains as barium carbonate. The remainder of the barium seems to fluctuate between oxide and peroxide, while a variable portion of the ruthenium is oxidized. The analyses show conclusively that six atoms of carbon are present in the salt derived from the nitrosochloride, hence one cyanogen group cannot be replaced by the nitroso group.

The results of several analyses are as follows:

	Theory for $Ba_2Ru(CN)_6$, $6H_2O$.	Found. From $RuCl_3$ and KCN sol.	From $RuCl_3NO$ by fusion.			From $RuCl_3NO$ by solution.		
		I.	II.	III.	IV.	V.	VI.	VII.
Barium	42.90	....	....	....	42.46	43.32	42.27	42.54
Ruthenium	15.86	16.41 (with SiO_2)	15.67	....	15.72	17.92 (with SiO_2)	15.80	15.60
$5\frac{1}{2}H_2O$ (100°)	15.67	15.67	15.63	....	15.68	....	....	15.53
$6H_2O$ (200°)	16.83	16.68	16.85	...	16.69	16.71	16.56	16.68
5 C	9.37	....	....	....	....	....	....	....
6 C	11.23	....	....	....	....	....	....	....
C from combustion	...	....	....	9.91	9.16	9.96	....	9.98
C in residue	....	....	....	2.65	2.03	....	....	2.30
Total carbon	....	....	....	12.56	11.19	....	....	12.28

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA., June, 1896.

DIPYRIDINE METHYLENE IODIDE AND THE NON-FORMATION OF THE CORRESPONDING MONOPYRIDINE PRODUCTS.[1]

By S. H. Baer and A. B. Prescott.
Received September 7, 1896.

THE addition compound of pyridine and methylene iodide was formed in different ways, varying the conditions of mass, temperature, pressure, and time, as follows. The method of preparation recommended is that of No. V.

Preparation I.—Pyridine and methylene iodode in equimolecular proportions, reacting at laboratory temperature, for two days, form a dark-red crystalline mass. This was washed in cold alcohol, which does not dissolve it.

Preparations II and III.—The same proportions (those of a monopyridine product) were taken in reaction at 120° C. The methyl iodide for I and II was colored with free iodine, that for III was obtained colorless by distillation in vacuum. In each case the crystals, washed with cold alcohol, were dark-red. This color was not affected by treating the crystals with thiosulphate solution, and therefore not due to free iodine or to periodides.

Preparation IV.—By reaction of colorless methylene iodide, in the same proportions, with the pyridine, but without heat, an orange precipitate settles slowly. This was washed as the others.

Preparation V.—Pyridine of boiling point 118° C., and methylene iodide either colorless or tinged with iodine, in about equal molecular quantities, are placed in a flask, alcohol in volume equal to the two reacting materials is added, a return-condenser adjusted, and the heat of a water-bath applied for an hour. On cooling, long yellow needles separate out. To purify further, dissolve in hot fifty per cent. alcohol, cool, and add a little ether, when fine crystals are formed.

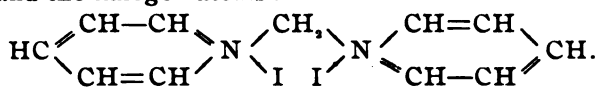
So obtained, the product is in fine needles, of yellow color, decomposing, not melting, at 220° C.; soluble in water, from which it crystallizes at 0° C.; insoluble in cold alcohol, sparingly soluble in hot alcohol; insoluble in ether, or chloroform, or benzene, or amyl alcohol; sparingly soluble in methyl alcohol.

Analysis gave us percentages as follows:

	Calculated for $(C_5H_5N)_2CH_2I_2$.	Found. I.	II.	III.	IV.	V.
I	59.61	58.95	58.91	57.98	58.4	59.6
N	6.57	....	....	....	...	6.72

[1] Read at the Buffalo meeting of the American Association for the Advancement of Science.

The product, therefore, not quite pure in the first four experimental preparations, is substantially the same under the different conditions employed, and with whatever excess of the diiodomethane, is always the dipyridine addition compound. And its formula, agreeing with those of its bromine homologues,[1] may be confidently written, to express the relations of the methylene group and the halogen atoms :



Kleine found[2] that trimethylamine, in combination with dihalogen substituted hydrocarbons, forms both the monammonium and the diammonium products, the former prevailing, especially when there are not more than two atoms of carbon in the halide.

It seemed now desirable to subject pyridine to various conditions of additive reaction with various dihalides, in order to know whether it can in any case form such monamine compounds as the fatty amines sometimes form.[3] Pyridine and ethylene bromide, in equal molecular proportions, were digested together in a sealed tube for two weeks, when the entire content, a crystalline mass, was dissolved in hot alcohol of ninety-five per cent., and fractionally crystallized in successive crops, washing each with cold absolute alcohol. These crops of crystals gave, of bromine, respectively, 46.15, 46.15, 46.18, and 46.03 per cent., the calculated per cent. in $(C_5H_5N)_2C_2H_4Br_2$ being 46.21.

Next pyridine with excess of ethylene bromide was digested in a pressure flask, in water-bath, with agitation. The crystallized product gave 46.26 per cent. of bromine. Finally dipyridine ethylene bromide was heated with excess of ethylene bromide in a sealed tube to 170° C. There was some charring in the mixture. By recrystallizing from it a product was obtained which gave 45.84 per cent. of bromine.

Dipyridine ethylene bromide crystallizes in colorless plates, insoluble in ether, and melting with decomposition at 295° C.

UNIVERSITY OF MICHIGAN.

1 The ethylene bromide, (Hofmann) Davidson, 1861 : *Proc. Roy. Soc.*, page 261 ; The trimethylene bromide, Flintermann and Prescott, 1895 : *J. Am. Chem. Soc.*, **18**, 28.

2 G. Kleine, 1894 : *Chem. Centrbl.*, page 161.

3 This in continuation of the inquiry of Flintermann and Prescott, 1895 : *J. Am. Chem. Soc.*, **18**, 33.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. No. 13.]

DETERMINATION OF THE ATOMIC MASSES OF SILVER, MERCURY AND CADMIUM BY THE ELECTROLYTIC METHOD.[1]

BY WILLETT LEPLEY HARDIN.

Received September 26, 1896.

INTRODUCTION.

A glance at the literature on the determinations of the atomic masses of silver, cadmium and mercury will show that, with the exception of cadmium, the electrolytic method has not been tried. Aside from the fact that certain errors involved in the washing and drying of the precipitates are eliminated by this method, its simplicity at once gives it preference over the usual methods of gravimetric determinations. Inasmuch as these three metals are completely precipitated from certain of their solutions by the electric current, and as it is desirable to determine the atomic mass of any element by different methods, it was thought advisable to apply this method in a redetermination of the atomic masses of these elements.

GENERAL CONSIDERATIONS.

Before taking up the different metals separately, the following general considerations may be mentioned :

1. A careful preliminary study was made in the selection of compounds. Some compounds, which from a theoretical standpoint seemed to offer certain advantages, were found by experiment not to meet the requirements of exact determinations. Salts which can be sublimed were used whenever possible ; and in all cases only those salts were used which form well defined crystals.

2. All reagents used were either prepared or purified by myself and carefully tested for impurities.

3. The metals were deposited in platinum dishes of about 200 cc. capacity and about sixty-five grams in weight. When the precipitation was complete, before interrupting the current, the

[1] From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D., 1896.

solution was siphoned from the platinum dish, pure water being added at the same time; this was continued until the solvent used was completely removed from the dish. The current was then interrupted and the deposit washed several times with boiling water, with the hope of removing any occluded hydrogen. After drying, the dishes were placed in a vacuum desiccator over anhydrous calcium chloride and allowed to remain in the balance room until their temperature was the same as that of the room. Atmospheric dust was excluded from the platinum dishes during the process of deposition by means of two glass plates which formed a complete cover; the moisture which collected on this cover was washed back into the dish from time to time. The dishes were handled with nickel tongs tipped with rubber.

4. The balance used was made expressly for this work by Henry Troemner, of Philadelphia. The beam and pans were made of aluminum, the beam being about twenty centimeters long. The framework was plated with gold to prevent corrosion. The sensibility for different loads and the ratio of the length of the two arms were carefully determined. The balance is sensitive to the fortieth of a milligram, and the sensibility is almost independent of the load up to seventy-five grams. The difference in the length of the two arms is so slight that no correction need be applied. The balance was kept in a large quiet room of nearly constant temperature.

The larger weights used were made of brass and the fractions of a gram made of platinum. The weights were all previously compared against each other and standardized with reference to the largest weight. The small corrections found in comparing them were tabulated and applied to all results. The weighings were made by the method of oscillations. The temperature and barometic pressure were noted at the time of each weighing, and all weighings were reduced to a vacuum standard. As the density of the atmosphere at the time of weighing the empty platinum dish was different from that at the time of weighing the dish and deposit together, the following formula was applied to obtain the weight of the deposit *in vacuo*:

$$\left[\text{Weight of (dish + deposit)} - \frac{\text{weight of dish}\left(1+\frac{\lambda}{\Delta}-\frac{\lambda}{f}\right)}{1+\frac{\lambda'}{\Delta}-\frac{\lambda'}{f}}\right]$$

$$\times\left[1+\frac{\lambda'}{\Delta'}-\frac{\lambda'}{f}\right] = \text{weight of deposit } \textit{in vacuo}.$$

Where λ = density of air at the time of weighing the empty dish.

λ' = density of air at the time of weighing the dish + deposit.

Δ = density of platinum dish.

Δ' = density of metallic deposit.

f = density of weights.

As the weights were all standardized with reference to the hundred-gram brass weight, it is evident that they must all be calculated as having the same density, equal to that of brass.

5. The atomic masses of the different elements involved in the calculation of results were taken from Clarke's latest report.[1]

PART I.

DETERMINATION OF THE ATOMIC MASS OF SILVER.

The mean of all the earlier determinations, as calculated by Clarke, gives 107.923 for the atomic mass of silver; a result almost identical with the mean (107.93; O = 16) of the determinations of Stas.

PREPARATION OF PURE METALLIC SILVER.

The silver used in this work was purified by the Stas method. Two hundred grams of silver, about ninety-nine per cent. pure, were dissolved in dilute hot nitric acid. The solution was evaporated to dryness, the nitrate heated to fusion and maintained in a fused condition until the oxides of nitrogen were no longer evolved. The residue, after cooling, was dissolved in as little cold water as possible, and after standing forty-eight hours the solution was filtered through a double filter to remove any suspended matter. The clear solution was then diluted with thirty times its volume of distilled water, and to it was added an

[1] *J. Am. Chem. Soc.*, 18, 197.

excess of pure hydrochloric acid. The silver chloride which separated was allowed to subside and was then thoroughly washed by decantation, at first with water containing a little hydrochloric acid, and finally with pure water. The precipitate was then collected on a cheese cloth filter, pressed strongly and allowed to dry. When perfectly dry, the silver chloride was powdered finely and digested for three days with aqua regia; it was then thoroughly washed by decantation with distilled water. After obtaining the pure chloride of silver, it was necessary to purify the caustic potash and milk sugar used in reducing the chloride to the metallic state. The caustic potash was heated to the boiling point and to it was added a concentrated solution of potassium sulphide to precipitate any heavy metals which might be present. The solution was filtered and the filtrate digested for some time with freshly precipitated silver oxide and again filtered to remove the excess of potassium sulphide. The milk sugar was purified in a similar manner. The silver chloride was then placed in large porcelain dishes and covered with a solution of caustic potash and milk sugar. The dishes were placed on a water-bath and heated to a temperature of 70°–80° until the reduction to finely divided metallic silver was complete. The alkaline solution was then poured off, and the gray metallic silver was washed with distilled water until the alkaline reaction disappeared. The metal was then digested with pure dilute sulphuric acid, and finally washed with dilute ammonia water. The silver thus obtained was mixed, when dry, with five per cent. of its weight of fused borax containing ten per cent. of pure sodium nitrate. The mixture was fused in a clay crucible and the silver poured into a mold. The metal obtained in this way was almost snow white in appearance, and dissolved completely in nitric acid to a colorless solution.

PREPARATION OF PURE NITRIC ACID.

To obtain pure nitric acid, one-half liter of the commercial C. P. acid was mixed with an equal volume of concentrated C. P. sulphuric acid and distilled from a retort provided with a knee tube and condenser. The first portion of the distillate was rejected. The process was stopped when half of the

nitric acid present had been distilled over. The distillate was mixed with an equal volume of pure sulphuric acid and redistilled. The second distillate was collected in a flask, the mouth of which was closed with glass wool. When the process was complete, the flask was closed with a doubly perforated cork and placed in a water-bath at a temperature of 40°. A current of pure dry air was then conducted through the acid to remove any oxides of nitrogen. The acid was kept in a dark place.

EXPERIMENTS ON SILVER OXIDE.

If pure, dry silver oxide could be prepared, the atomic mass of silver could be compared directly with that of oxygen. A large number of experiments were made on this compound with the hope of determining the ratio of the atomic masses of these two elements.

PREPARATION OF SILVER OXIDE.

A portion of the pure metallic silver was dissolved in pure dilute nitric acid and the solution evaporated to crystallization. The crystals of silver nitrate were dissolved in pure water and to the solution was added a solution of pure sodium hydroxide, prepared by throwing pieces of metallic sodium on distilled water in a platinum dish. The twenty-five grams of silver oxide prepared in this way were washed by decantation with twenty liters of water. The material was then dried at the ordinary temperature, after which it was finely powdered and dried for twenty-four hours in an air-bath at 100°. The oxide was kept in a weighing tube in a dark place.

Several analyses were made by dissolving a weighed portion of the material in pure potassium cyanide, electrolyzing the solution and weighing the resulting metallic silver. The observations invariably gave less than ninety-five for the atomic mass of silver. The oxide was redried at a temperature of 125° and analyzed as before, but the quantity of silver obtained was far below that calculated for the compound Ag_2O. Observations were also made on material dried at 140° and 150°. The results showed that it was impossible to prepare the silver oxide in a pure, dry condition.

After making these observations, my attention was called to an article by M. Carey Lea,[1] in which were given the results of a series of analyses of silver oxide dried at different temperatures varying from 100° to 170°. These observations prove conclusively that oxygen is given off at a much lower temperature than that required to remove the last traces of moisture. From these observations and the results obtained by myself, it was evident that any further attempt to determine the atomic mass of silver from the oxide would be useless.

Although no careful study was made as to the nature of this compound, it might be added that, from my own observations, it seems very probable that the oxide contains some hydrogen in the form of hydroxyl.

FIRST SERIES.

EXPERIMENTS ON SILVER NITRATE.

The nitrate of silver seems to fulfil the conditions necessary for accurate analyses, inasmuch as it is stable and crystallizes in well defined crystals which can be fused without decomposition.

PREPARATION OF SILVER NITRATE.

The material used in these experiments was prepared by dissolving pure silver in pure aqueous nitric acid in a porcelain dish. An excess of silver was used, and after complete saturation the solution was poured off from the metal into a second dish and evaporated to crystallization. The perfectly transparent, rhombic plates of silver nitrate which separated were dissolved in pure water and recrystallized. The crystals were then carefully dried, placed in a platinum crucible which rested in a larger platinum dish and gradually heated to fusion. After cooling, the perfectly white opaque mass was broken up and placed in a ground-glass stoppered weighing tube and kept in a desiccator in a dark place.

MODE OF PROCEDURE.

The platinum dish in which the deposit was made was care-

[1] *Am. J. Sci.*, 44, 240.

fully cleaned with nitric acid and dried to constant weight. It was then placed in a desiccator over anhydrous calcium chloride, and this, together with the desiccator containing the tube of silver nitrate, was placed in the balance room, where they were allowed to remain until their temperatures were the same as that of the room. After weighing the platinum dish, the tube of silver nitrate was weighed and part of the salt removed to the dish, after which the tube was reweighed. The difference in the two weighings, of course, represented the weight of silver nitrate used in the experiment. Enough water to dissolve the nitrate was added to the dish, and then a solution of potassium cyanide, made by dissolving seventy-five grams of pure potassium cyanide in one liter of water, was added until the silver cyanide first formed was completely dissolved. The dish was then filled to within a quarter of an inch of the top with pure water and the solution electrolyzed with a gradually increasing strength of current. The following table will show the strength of current and the time through which it acted :

Time of action.	Strength of current.
2 hours	$N.D_{100} = 0.015$ amperes.
4 "	$N.D_{100} = 0.030$ "
6 "	$N.D_{100} = 0.075$ "
4 "	$N.D_{100} = 0.150$ "
4 "	$N.D_{100} = 0.400$ "

By gradually increasing the strength of current in this way the silver came down in a dense, white deposit. When the deposition was complete, before interrupting the current, the liquid was siphoned from the dish, pure water being added at the same time. This was continued until the cyanide was completely removed. The dish with the deposit was washed several times with boiling water and carefully dried. It was then placed in a desiccator and allowed to remain in the balance room until its temperature was the same as that of the room, when it was reweighed.

Weight of platinum dish = 71.27302 grams.

Weight of silver nitrate = 0.31198 grams.

Temperature, 22°.

Barometric pressure, 770 mm.

Weight of platinum dish + silver deposit = 71.47104 grams.

Temperature, 22°.
Barometric pressure, 760 mm.
Density of silver nitrate = 4.328.
" " brass weights = 8.5.
" " platinum dish = 21.4.
" " metallic silver = 10.5.
" " atmosphere at the time of weighing the empty dish and silver nitrate = 0.001212.
" " atmosphere at the time of weighing the platinum dish + silver deposit = 0.001196.

Computing on this basis we have the following:

$$0.31198\left(1+\frac{0.001212}{4.328}-\frac{0.001212}{8.5}\right) = 0.31202 = \text{weight of } AgNO_3 \textit{ in vacuo}.$$

$$71.27302\left[\frac{1+\frac{0.001212}{21.4}-\frac{0.001212}{8.5}}{1+\frac{0.001196}{21.4}-\frac{0.001196}{8.5}}\right] = 71.27291 = \text{weight of platinum dish at } 22° \text{ and } 760 \text{ mm.}$$

$71.47104 - 71.27291 = 0.19813$ = weight of deposit at 22° and 760 mm.

$$0.19813\left(1+\frac{0.001196}{10.5}-\frac{0.001196}{8.5}\right) = 0.19812 = \text{weight of deposit } \textit{in vacuo}.$$

Taking O = 16 and N = 14.04, the atomic mass of silver =
$$\frac{0.19812 \times 62.04}{(31202 - 19812)} = 107.914.$$

Ten observations on silver nitrate computed in the foregoing manner are as follows:

	Weight of $AgNO_3$. Gram.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.31202	0.19812	107.914
2	0.47832	0.30370	107.900
3	0.56742	0.36030	107.923
4	0.57728	0.36655	107.914
5	0.69409	0.44075	107.935
6	0.86367	0.54843	107.932
7	0.86811	0.55130	107.960

	Weight of $AgNO_3$. Gram.	Weight of Ag. Gram.	Atomic mass of silver.
8	0.93716	0.59508	107.924
9	1.06170	0.67412	107.907
10	1.19849	0.76104	107.932

Mean = 107.924
Maximum = 107.960
Minimum = 107.900

Difference = 0.060
Probable error = ±0.005

Computing the atomic mass of silver from the total quantity of material used and metal obtained, we have 107.926.

SECOND SERIES.

EXPERIMENTS ON SILVER ACETATE.

The fact that silver forms well crystallized salts with a number of organic acids makes the comparison of the atomic mass of silver with the combined atomic masses of carbon, hydrogen, and oxygen, a matter of no great difficulty. From certain preliminary experiments, the acetate of silver seemed to fulfill the conditions necessary for accurate determinations.

PREPARATION OF SILVER ACETATE.

The purest commercial sodium acetate was dissolved in water, the solution filtered and recrystallized. After three crystallizations the material was dissolved in pure water, and to the rather concentrated solution was added a solution of silver nitrate, prepared in the manner already indicated. The white curdy precipitate which separated, after washing with cold water, was dissolved in hot water, the solution filtered and evaporated to crystallization. The silver acetate separated in brilliant sword-shaped crystals. After pouring off the solution the crystals were quickly rinsed with cold water and placed between filters to remove the adhering moisture. The material was allowed to remain in contact with the filters only for a short time. It was then placed in a platinum dish, and when apparently dry the crystals were broken up into a finely divided condition and dried forty-eight hours in a vacuum desiccator. This work was carried on in a darkened room, and the silver acetate obtained was

placed in a weighing tube, and kept in a desiccator in a dark place.

MODE OF PROCEDURE.

The method of operation was similar to that described under silver nitrate. After weighing the silver acetate, its aqueous or cyanide solution was electrolyzed and the weight of the resulting metallic silver determined. The results obtained from the aqueous solution were sometimes vitiated by the separation of silver peroxide at the anode. To prevent this, potassium cyanide was sometimes added. The results, however, from the two solutions were practically the same when no peroxide separated. From the aqueous solution the silver was deposited in a crystalline form. The strength of current and time of action were the same as for silver nitrate.

Ten observations on silver acetate reduced to a vacuum standard on the basis of

3.241 = density of silver acetate,
10.5 = " metallic silver,
24.4 = " platinum dish,
8.5 = " weights,

and computed for the formula $AgC_2H_3O_2$, assuming the atomic masses of carbon, hydrogen and oxygen to be 12.01, 1.008 and 16, respectively, are as follows:

	Weight of $AgC_2H_3O_2$. Grams.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.32470	0.20987	107.904
2	0.40566	0.26223	107.949
3	0.52736	0.34086	107.913
4	0.60300	0.38976	107.921
5	0.67235	0.43455	107.896
6	0.72452	0.46830	107.916
7	0.78232	0.50563	107.898
8	0.79804	0.51590	107.963
9	0.92101	0.59532	107.925
10	1.02495	0.66250	107.923

Mean = 107.922
Maximum = 107.963
Minimum = 107.896

Difference = 0.067
Probable error = ± 0.005

Computing from the total quantity of material used and metal obtained we have 107.918 for the atomic mass of silver.

EXPERIMENTS ON SILVER SUCCINATE.

Silver succinate was prepared in a manner similar to that of silver acetate. The commercial C. P. succinic acid was recrystallized three times; the ammonium salt was then prepared and its aqueous solution precipitated with a solution of pure silver nitrates. The precipitate of silver succinate was thoroughly washed by decantation with pure water and carefully dried. After drying for several hours in an air-bath at 50°, the material was ground in an agate mortar to a finely divided powder, and was then redried for twenty-four hours in an air-bath at a temperature of 60°. The white powder obtained in this way was placed in a weighing tube and kept in a desiccator.

The method of analysis was similar to that of silver acetate. A weighed portion of the material was dissolved in a little potassium cyanide in a platinum dish. After diluting with pure water, the solution was electrolyzed and the resulting deposit weighed. The strength of current and time of action were the same as for silver nitrate. The results computed for the formula $C_4H_4O_4Ag_2$ were not constant, and were invariably from one to two units lower than those obtained from silver nitrate and silver acetate. The material was then dried at a temperature of 75°, but the results obtained were not satisfactory.

The two most probable causes for these low results are:

First, the difficulty of removing the last traces of impurities from a precipitate like that of silver succinate. The experience throughout this work has been, that, to remove all the impurities from a finely divided precipitate by washing is almost impossible.

Second, the difficulty met in drying material of this kind. This same difficulty was met in the experiments on silver oxide which, as shown by Lea, retained moisture up to 165°.

THIRD SERIES.

EXPERIMENTS ON SILVER BENZOATE.

The preceding work on silver acetate and silver succinate shows the necessity of selecting compounds which form well defined crystals. Perhaps no organic salt of silver fulfils the

conditions necessary for accurate analyses better than silver benzoate.

PREPARATION OF SILVER BENZOATE.

The purest commercial benzoic acid was resublimed three times from a porcelain dish into a glass beaker. The product thus obtained was dissolved in pure aqueous ammonia and the solution evaporated to crystallization. The ammonium salt was then dissolved in distilled water and to the solution was added a solution of pure silver nitrate. The white precipitate of silver benzoate which separated was washed with cold water; it was then dissolved in hot water, the solution filtered, and evaporated to crystallization. The salt separated in fine needles, which clung together in arborescent masses. After removing the liquid from the beaker, the crystals were quickly rinsed with cold water and placed between filters to remove the adhering moisture. When apparently dry they were broken up into small fragments and dried forty-eight hours in a vacuum desiccator. The material was then placed in a glass stoppered weighing tube and kept in a dark place.

MODE OF PROCEDURE.

The details of the method of operation are the same as those given under silver nitrate. A weighed portion of the material was dissolved in a dilute solution of potassium cyanide in a platinum dish. The solution was then electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for silver nitrate.

Before the results could be reduced to a vacuum standard it was necessary to determine the specific gravity of silver benzoate. This was done by means of a specific gravity bottle, the liquid used being chloroform. The mean of two determinations gave 2.082 for the specific gravity of silver benzoate.

Ten results on this compound, reduced to a vacuum standard on the basis of

2.082 = density of silver benzoate,
10.5 = " " metallic silver,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $C_7H_5AgO_2$, assuming 12.01, 1.008, and 16 to be the atomic masses of carbon, hydrogen and oxygen, respectively, are as follows:

	Weight of $C_7H_5AgO_2$. Grams.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.40858	0.19255	107.947
2	0.46674	0.21999	107.976
3	0.48419	0.22815	107.918
4	0.62432	0.29418	107.918
5	0.66496	0.31340	107.964
6	0.75853	0.35745	107.935
7	0.76918	0.36247	107.936
8	0.81254	0.38286	107.914
9	0.95673	0.45079	107.908
10	1.00840	0.47526	107.962

Mean = 107.938
Maximum = 107.976
Minimum = 107.908

Difference = 0.068
Probable error = ±0.005

Computing from the total quantity of material used and metal obtained we have 107.936 for the atomic mass of silver.

SUMMARY.

In discussing the work on the atomic mass of silver, two possible sources of error suggest themselves.

First, the hydrogen which is continually being set free in the process of electrolysis may, in part, be occluded by the metallic silver. As already pointed out, the metallic deposits were washed several times with boiling water, with the hope of removing any occluded gases; but whether this effected a complete removal of all the occluded gases was not determined.

Second, the condensation of moisture on the platinum dish might be urged as a possible source of error. But it must be remembered that the dish was dried in the same manner each time and kept for several hours in a desiccator, and that the atmosphere inside the balance was kept dry by means of several beakers of anhydrous calcium chloride, and that the temperature of the balance room throughout the work was almost constant. Under these conditions there is but little chance of error from

different amounts of moisture condensed. Moreover, the variation in the different weighings of the same dish was very slight.

The advantages of the method are evident.

First, the great advantage of the method is its extreme simplicity.

Second, the nature of the compounds used and of metallic silver renders them well adapted to weighing.

Third, the method was such as to eliminate the errors incident to the ordinary gravimetric methods of analysis.

Of the three series, the first is probably entitled to the greatest weight. That the silver nitrate was pure and free from moisture seems beyond question. However, the close agreement of the last two series with the first indicates that the acetate and benzoate of silver were also free from moisture.

Giving equal weight to each of the three series, we have the following as the general mean computed from the separate observation :

	Atomic mass of silver.
First series	107.924
Second "	107.922
Third "	107.938
General mean =	107.928

Computing the general mean from the total quantities of material used and metal obtained we have :

	Atomic mass of silver.
First series	107.926
Second "	107.918
Third "	107.936
General mean =	107.927

Combining this with the first general mean we have 107.9275 as the final result for the atomic mass of silver.

PART II.

DETERMINATION OF THE ATOMIC MASS OF MERCURY.

From all the earlier determinations Clarke gives 200 as the

most probable value for the atomic mass of mercury, assuming oxygen equal to 16.

EXPERIMENTS ON MERCURIC OXIDE.

A large number of experiments were made with a view of determining the ratio of mercury to oxygen in mercuric oxide. The method proved to be unsatisfactory, although, apparently very good results were obtained in some preliminary experiments. The cause of this close agreement of results will be explained in the details of the work.

PREPARATION OF PURE MERCURIC OXIDE.

The purest commercial mercuric chloride was carefully sublimed from a porcelain dish into a glass funnel. The sublimed portion was dissolved in water, the solution filtered, and evaporated to crystallization. The crystals were then thoroughly dried and carefully resublimed. The product obtained in this way consisted of white crystalline leaflets which dissolved completely in water. Pure sodium hydroxide was then prepared by throwing pieces of metallic sodium on pure water contained in a platinum dish. To the pure sodium hydroxide was added a solution of mercuric chloride, the former always being in excess. The yellow mercuric oxide which separated was washed for several days by decantation with hot water. The material was then dried twenty-four hours in an air-bath at 105°.

MODE OF PROCEDURE.

In a series of preliminary experiments made in the spring of 1895, a weighed portion of mercuric oxide prepared in the above manner was dissolved in a dilute solution of potassium cyanide in a platinum dish. The solution was then electrolyzed and the weight of the resulting metallic mercury determined. Inasmuch as the results obtained in these preliminary experiments were not reduced to a vacuum standard, it was thought advisable to weigh the empty platinum dish after removing the metallic deposit in order that the two weighings might be made under approximately the same conditions. The results for the most part agreed very closely and differed very little from the results obtained by other methods. Six observations computed for the formula HgO, assuming the atomic mass of oxygen to be 16, are as follows:

	Weight of HgO. Gram.	Weight of Hg. Gram.	Atomic mass of mercury.
1	0.26223	0.24281	200.05
2	0.23830	0.22065	200.02
3	0.23200	0.21482	200.06
4	0.14148	0.13100	200.00
5	0.29799	0.27592	200.03
6	0.19631	0.18177	200.02

Mean = 200.03.

These results were selected from a larger series. After making the above observations it was noticed that the platinum dish had gradually decreased in weight throughout the work. This decrease in weight indicated that the mercury deposit had formed an amalgam with the platinum dish, which was soluble in hot nitric acid. To ascertain whether such was the case or not the platinum dish, after weighing, was filled with a solution of the double cyanide of mercury and potassium and the solution electrolyzed. On dissolving the mercury deposit in cold nitric acid a dark colored film remained on the sides of the dish. The dish was then carefully washed, dried and reweighed, and found to be heavier than at the beginning of the operation, showing that the mercury had not been completely removed. The dark film was then dissolved in hot nitric acid and the dish again weighed. This last weight being less than that at the beginning showed that some of the platinum had been dissolved from the dish. The nitric acid solution of the dark film was evaporated to dryness and ignited to remove the mercury. The residue was dissolved in aqua regia, the solution evaporated to dryness, and enough water added to dissolve the small residue. A little concentrated ammonium chloride was then added to the solution, and the double chloride of ammonium and platinum separated as a yellow crystalline powder. This proved conclusively that the mercury deposit had united with the platinum dish to form an amalgam which was soluble in hot nitric acid. Hence the results given for mercuric oxide are of no value in determining the atomic mass of mercury.

A series of careful experiments was then made on the oxide dried at different temperatures. To avoid any error from the

amalgam which formed with each deposit, the platinum dish was weighed at the beginning of each observation, the temperature and barometric pressure being noted at the same time. The results obtained from the oxide dried at a temperature of 105° gave from 180 to 185 for the atomic mass of mercury. The material was then dried at a temperature of 125°, but the increase in the amount of mercury obtained was very slight. Finally with material dried at 150°, the results obtained for the atomic mass of mercury were all below 195°.

The most probable causes for these low results are:

First, the difficulty of removing the last traces of alkalies from the mercuric oxide.

Second, the difficulty met in the complete removal of the moisture from an amorphous precipitate. This difficulty as well as the first was referred to in the experiments on silver oxide.

Third, mercuric oxide does not form a clear solution with potassium cyanide. There seems to be a slight reduction of the oxide to the metallic state. It is difficult to determine whether this reduced portion unites completely with the metallic deposit or is partially removed in the process of washing. The latter is probably true, and it may be that a different method of analysis would give more accurate results for this compound.

FIRST SERIES.

EXPERIMENTS ON MERCURIC CHLORIDE.

The material used in this series of experiments was prepared from the commercial C. P. mercuric chloride. The product was first dissolved in water, the solution filtered and evaporated to crystallization. The crystals were dried and carefully sublimed from a porcelain dish into a glass funnel. The sublimed portion was dissolved in water, the solution filtered and evaporated to crystallization. These crystals were dried as before and carefully resublimed. The material was then placed in a weighing tube and kept in a desiccator.

MODE OF PROCEDURE.

The method of operation was similar to that already described

under the different compounds of silver. A weighed portion of the mercuric chloride was dissolved in a little potassium cyanide and the solution electrolyzed. The deposit was washed and dried and handled in every way like the deposits of silver. The strength of the current and time of action were as follows:

Time of action.	Strength of current.
4 hours	$N.D_{100} = 0.02$ amperes.
6 "	$N.D_{100} = 0.05$ "
6 "	$N.D_{100} = 0.10$ "
6 "	$N.D_{100} = 0.30$ "

A current of gradually increasing strength deposits the mercury in extremely small globules, which can be washed and handled more easily than the larger globules obtained by using a strong current at first. In cases where more than one-half gram of metal was deposited the strong current was allowed to act two hours longer.

Ten results on mercuric chloride reduced to a vacuum standard on the basis of

5.41 = density of mercuric chloride,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed from the formula $HgCl_2$, assuming 35.45 to be the atomic mass of chlorine, are as follows:

	Weight of $HgCl_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.45932	0.33912	200.030
2	0.54735	0.40415	200.099
3	0.56002	0.41348	200.053
4	0.63586	0.46941	199.947
5	0.64365	0.47521	200.026
6	0.73281	0.54101	199.988
7	0.86467	0.63840	200.838
8	1.06776	0.78825	199.946
9	1.07945	0.79685	199.917
10	1.51402	1.11780	200.028

Mean = 200.006
Maximum = 200.099
Minimum = 199.917

Difference = 0.182
Probable error = ±0.011

Computing from the total quantity of material used and metal obtained we have 199.996 for the atomic mass of mercury.

SECOND SERIES.

EXPERIMENTS ON MERCURIC BROMIDE.

The bromine used in these experiments was prepared by distilling the commercial C. P. bromine twice over manganese dioxide. Any trace of chlorine which might be present would be removed by this method.

PREPARATION OF MERCURIC BROMIDE.

Fifty grams of metallic mercury were placed in a beaker and covered with water. Pure bromine was then added until the mercury was completely saturated. The contents of the beaker were then digested with hot water until the mercuric bromide dissolved; the solution was filtered and evaporated to crystallization. The white crystals of mercuric bromide which separated were thoroughly dried and carefully sublimed from a porcelain dish into a glass funnel. Only the middle portion of the sublimate was used in the experiments. The product obtained in this way consisted of brilliant crystalline leaflets which dissolved completely in water. The material was kept in a weighing tube in a desiccator.

MODE OF PROCEDURE.

The method of analysis was exactly like that described under mercuric chloride. A weighed portion of the mercuric bromide was dissolved in dilute potassium cyanide in a platinum dish. The solution was then electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for mercuric chloride.

Ten results on mercuric bromide reduced to a vacuum standard on the basis of

5.92 = density of mercuric bromide,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $HgBr_2$, assuming 79.95 to be the atomic mass of bromine, are as follows :

	Weight of $HgBr_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.70002	0.38892	199.898
2	0.56430	0.31350	199.876
3	0.57142	0.31750	199.938
4	0.77285	0.42932	199.832
5	0.80930	0.44955	199.814
6	0.85342	0.47416	199.911
7	1.11076	0.61708	199.869
8	1.17270	0.65145	199.840
9	1.26186	0.70107	199.899
10	1.40142	0.77870	199.952

Mean = 199.883
Maximum = 199.952
Minimum = 199.814

Difference = 0.138
Probable error = ±0.010

Computing from the total quantity of material used and metal obtained, the atomic mass of mercury is 199.885.

THIRD SERIES.

EXPERIMENTS ON MERCURIC CYANIDE.

A series of observations was made on several organic salts of mercury with a view of selecting a compound suitable for atomic mass determinations. Mercuric acetate and other similar salts were found to be unstable in the air and unsuited for accurate analyses. Mercuric cyanide, on the other hand, was found to be perfectly stable and to form well defined crystals.

PREPARATION OF HYDROCYANIC ACID.

Five hundred grams of potassium ferrocyanide were placed in a two liter retort connected with a condenser. A cooled mixture of 300 grams of pure sulphuric acid and 700 cc. of distilled water was then poured into the retort and the mixture carefully heated until the hydrocyanic acid was distilled over into the receiver. The product obtained was redistilled and used immediately in the preparation of mercuric cyanide.

PREPARATION OF MERCURIC CYANIDE.

Fifty grams of mercuric oxide, prepared as already described in the experiments on mercuric oxide, were dissolved in pure, warm hydrocyanic acid. The solution was then filtered and evaporated to crystallization. The transparent crystals of mercuric cyanide which separated were dissolved in pure water and recrystallized. The product obtained by the second crystallization was quickly rinsed with cold water and dried for six hours in an air bath at a temperature of 50°. The crystals were then ground to a finely divided powder in an agate mortar and redried for twenty-four hours in an air bath at a temperature of 55°. The dry, white powder was then placed in a weighing tube and kept in a desiccator.

MODE OF PROCEDURE.

The mode of procedure with mercuric cyanide was somewhat different from that of the preceding experiments, in that no potassium cyanide was used in preparing the solution for electrolysis. A weighed portion of the material was dissolved in pure water in a platinum dish. When the crystals had completely dissolved, the dish was filled to within a quarter of an inch of the top with water, after which one drop of pure sulphuric acid was added. The solution was then electrolyzed and the resulting metal weighed. The strength of the current and the time of action were the same as for merouric chloride. In the last four experiments, where rather large quantities of mercury were deposited, the strong current was allowed to act from two to six hours longer.

The results of ten experiments on mercuric cyanide, reduced to a vacuum standard on the basis of

4.0 = density of mercuric cyanide,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $Hg(CN)_2$, assuming 12.01 and 14.04 to be the atomic masses of carbon and nitrogen, respectively, are as follows :

	Weight of $Hg(CN)_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.55776	0.44252	200.063
2	0.63290	0.50215	200.092
3	0.70652	0.56053	200.038
4	0.80241	0.63663	200.075
5	0.65706	0.52130	200.057
6	0.81678	0.64805	200.103
7	1.07628	0.85392	200.077
8	1.22615	0.97282	200.071
9	1.66225	1.31880	200.057
10	2.11170	1.67541	200.077

Mean = 200.071
Maximum = 200.103
Minimum = 200.038

Difference = 0.065
Probable error = 0.005

From the total quantity of material used and metal obtained, the atomic mass of mercury is 200.070.

FOURTH SERIES.

According to Faraday's law the quantities of different metals deposited from their solutions by the same current are proportional to their equivalent weights. In this series of experiments an attempt was made to determine the ratio of the atomic mass of mercury to that of silver by passing the same current through the solutions of the two metals and weighing the two resulting deposits. If the proper conditions could be obtained, this would certainly be the simplest and most direct method for comparing the equivalent weights of different metals. But so many difficulties were met that the method on the whole was not satisfactory.

In the "Revision of the Atomic Weight of Gold,"[1] Mallet made use of this method, and in a series of careful preliminary experiments determined the conditions most favorable to its application. From a number of experiments made by passing the same current through two different solutions of copper sul-

[1] *Am. Chem. J.*, 12, 182.

phate, using pure electrotype copper for both anode and cathode in each solution, Mallet found:

First.—Other conditions being the same, the difference in the quantities of metal deposited from solutions of unequal concentrations was very slight and somewhat variable, but the tendency was toward a slightly larger quantity from the more concentrated solution.

Second.—With equal quantities of metal in the two solutions and unequal quantities of free acid, the difference in the results obtained were almost insignificant and somewhat variable in direction, the tendency being toward a slightly larger quantity from the less acid solution.

Third.—Other conditions being the same, a difference in the temperature of the two solutions invariably caused a slightly larger deposit from the cooler solution.

Fourth.—Other conditions being the same, a difference in the size of the copper plates, and hence a difference in the "current density," caused a slightly greater deposit on the smaller plate.

Fifth.—A difference in the distance between the two plates did not produce a constant difference of result, but the tendency was toward a slightly larger deposit on the cathode plate farther separated from its anode.

From the foregoing experiments it is evident that the conditions most favorable to this method are, that the two solutions should be equally concentrated, of the same temperature, and should contain equal amounts of free acid, or when the double cyanides are used, equal quantities of free potassium cyanide. And, moreover, that the two cathodes and also the two anodes should be of the same size, and that the distance between the anode and cathode should be the same in both solutions. These conditions were closely observed throughout this work.

ARRANGEMENT OF APPARATUS.

The deposits in this series of experiments were made in two platinum dishes of equal capacity and equal internal area. The anode in each case consisted of a coil of rather large platinum wire, the two coils being of the same shape and size. The dishes were insulated from each other by means of two glass stands.

The platinum coils were completely immersed in the solutions and the portion of the wire near the surface of the liquid was covered with paraffin to prevent surface contact. The current, after passing through the two solutions, was allowed to pass through a hydrogen voltameter in order that its strength might be observed at any time.

In the second arrangement of apparatus the platinum dishes were made the anodes, and two pieces of platinum foil of the same shape and size were used for the cathodes. The results, however, from this second arrangement were not as satisfactory as from the first.

MODE OF PROCEDURE.

A solution of the double cyanide of silver and potassium was placed in one of the platinum dishes and a solution of the double cyanide of mercury and potassium in the other. The quantities of silver and mercury present in their solutions were approximately proportional to their equivalent weights. Each solution contained a slight excess of potassium cyanide. The dishes were placed in their positions and the anodes immersed sometime before the current was allowed to act. When the temperature of the two solutions was the same as that of the room, the connection was made and the same current allowed to pass through the two solutions. The quantity of metal deposited was never allowed to exceed one-half of the metal present in the solution at first. Before interrupting the current, the solutions were siphoned from the two platinum dishes at the same time with two siphons of the same bore. The deposits were then washed several times with boiling water, carefully dried and their weights determined. Experiments were made with currents of different strength and with solutions of various degrees of concentration. The results obtained were far from being satisfactory. The strength of current which seemed best adapted to the work was that which deposited about one-tenth of a gram of silver per hour.

From a large number of experiments, only seven results were obtained which seem of any value in determining the atomic mass of mercury. And it must be added that many others were

From the total quantities of material used and metal obtained, the general mean is :

	Atomic mass of mercury.
First series	199.996
Second "	199.885
Third "	200.070
Fourth "	199.971
General mean =	199.981

Combining this with the first general mean we have :

	Atomic mass of mercury.
First general mean =	199.989
Second " " =	199.981
Most probable mean of all the results =	199.985

or 200 for the atomic mass of mercury.

PART III.

DETERMINATION OF THE ATOMIC MASS OF CADMIUM.

Nine experimenters have determined the atomic mass of cadmium by many different methods, but the large variations in the results given by different chemists leave the true value of this constant still uncertain.

Stromeyer[1] gave no details of his method of operation, but found that 100 parts of cadmium combined with 14,352 parts of oxygen. On the basis of $O = 16$, this ratio gives 111.483 for the atomic mass of cadmium. This result is much lower than those obtained by other experimenters and is perhaps only of historical interest.

In a series of nine experiments, Von Hauer[2] determined the ratio of cadmium sulphate to cadmium sulphide. The sulphate used was purified by repeated recrystallizations and was finally dried at a temperature of 200°. After weighing the sulphate was always dried a second time and reweighed. The two weighings never differed as much as one milligram. The sulphide obtained was in each case tested for sulphate. The reduction of the sulphate to sulphide was accomplished by heating

[1] Berzelius' Lehrbuch, 5th Ed., 3, 1219.

[2] *J. prakt. Chem.*, 72, 350.

the sulphate in a current of dry hydrogen sulphide under pressure. The mean of nine observations computed on the basis › $O = 16$ and $S = 32.06$ gives 111.93 for the atomic mass of cadmium. Considering the large quantity of material used each time and the precautions taken to insure accuracy, there seems to be little objection to the method.

Dumas[1] determined the ratio of cadmium chloride to metallic silver by titrating a solution containing a weighed quantity of cadmium chloride with a silver nitrate solution of known strength. The cadmium chloride was prepared by dissolving metallic cadmium in boiling hydrochloric acid. The solution was evaporated to dryness and the chloride fused for six hours in a current of hydrochloric acid gas. The mean of six determinations gives 112.24 for the atomic mass of cadmium ($O = 16$).

$$\begin{array}{lr} \text{Maximum result, Cd} = & 112.759 \\ \text{Minimum '' Cd} = & 111.756 \\ \hline \text{Difference} = & 1.003 \end{array}$$

This large variation in the results obtained indicates the presence of impurities in the material used. In the first three experiments the cadmium was not purified; the mean of these three is Cd = 112.476. The metal used in the last three experiments was considered by Dumas to be absolutely pure; the mean of the last three results is Cd = 112.007. From the degree of purity of the cadmium chloride used in the different experiments, Dumas was inclined to reject the higher results and concluded that the true atomic mass of cadmium was about 112.

Lensen[2] prepared pure cadmium oxalate by precipitating a solution of cadmium chloride, purified by repeated crystallization, with pure oxalic acid. The precipitate was washed and carefully dried at a temperature of 150°. The mean of three results obtained by converting a weighed portion of the oxalate to oxide gives 112.06 for the atomic mass of cadmium ($O = 16$). The small quantity of material used in the different experiments is somewhat objectionable.

[1] *Ann. chim. phys.*, [3], 55, 158.
[2] *J. prakt. Chem.*, 79, 281.

Huntington,[1] under the direction of Cooke, determined the ratio of cadmium bromide to silver bromide and also the ratio of cadmium bromide to metallic silver. The bromide used was prepared by dissolving cadmium carbonate, which had been carefully purified, in pure hydrobromic acid. The product obtained was dried at a temperature of 200° and finally sublimed in a porcelain tube in a current of dry carbon dioxide. In the first series of experiments the silver bromide corresponding to the cadmium bromide used was weighed. The mean of eight determinations computed from the total quantity of material used and silver bromide obtained, on the basis of Ag = 107.93 and Br = 79.95 is Cd = 112.24. In the second series of experiments the quantity of metallic silver required to precipitate a known quantity of cadmium bromide was determined. The mean of eight determinations computed as in the first series gives 112.245 for the atomic mass of cadmium. The separate determinations in both series agree very closely.

Partridge[2] made three series of determinations. The first depended upon the conversion of cadmium oxalate into oxide, the second, on the reduction of the sulphate to sulphide, and the third, on the conversion of the oxalate into sulphide. The cadmium used in these experiments was purified by distilling twice *in vacuo*. Ten observations on the conversion of the oxalate into oxide, computed on the basis of O = 16 and C = 12, give 111.801 as a mean for the atomic mass of cadmium. Recalculated by Clarke,[3] on the basis of O = 16 and C = 12.005, the atomic mass of cadmium becomes 111.818. The mean of ten results obtained by reducing the sulphate to sulphide, computed on the basis of O = 16 and S = 32, gives 111.797 for the atomic mass of cadmium. Recalculated by Clarke on the basis of O = 16 and S = 32.074, the atomic mass of cadmium is 111.711. In the third series the oxalate of cadmium was converted into sulphide by heating in a current of dry hydrogen sulphide. The mean of ten determinations, computed on the basis of O = 16 and S = 32, gives 111.805 for the atomic mass of cadmium.

1 *Proc. Amer. Acad.*, 17, 28.
2 *Am. J. Sci.*, [3], 40, 377.
3 *Am. Chem. J.*, 13, 34.

Recalculated by Clarke on the basis of O = 16 and S = 32.074, the mean becomes 111.589. Partridge gives 111.8 for the atomic mass of cadmium, as a mean of the three series. If the higher values for carbon and sulphur be introduced this value becomes somewhat lower.

Jones[1] determined the atomic mass of cadmium by two different methods. The first was based on the conversion of the metal into oxide, and the second on the conversion of the oxalate into oxide. The cadmium used was distilled six times *in vacuo*. The last distillate was tested spectroscopically and found to be free from impurities. In the first series of experiments a weighed portion of the pure metal was dissolved in pure nitric acid in a porcelain crucible. The solution was evaporated to dryness and the resulting cadmium nitrate ignited to oxide. The final decomposition was accomplished by means of a blast lamp. Reducing gases were carefully excluded from the crucible during the process of ignition. The weighings were all made against a tared crucible. The mean of ten observations, computed on a basis of O = 16 gives 112.07 for the atomic mass of cadmium. The different determinations agree very closely. In the second series of experiments cadmium oxalate, prepared by precipitating pure cadmium nitrate with pure oxalic acid, was converted into oxide. The material was carefully ignited until the oxalate was decomposed; it was then treated with nitric acid and again ignited in a manner similar to that described in the first series. The mean of five determinations computed on the basis of O = 16 and C = 12.003 is Cd = 111.032. From all the observations, Jones concludes that 112.07 represents very closely the atomic mass of cadmium (O = 16).

Lorimer and Smith[2] determined the ratio of the atomic mass of cadmium to that of oxygen by dissolving pure cadmium oxide in potassium cyanide and electrolyzing the solution. To obtain pure material, the commercial cadmium was dissolved in nitric acid and the solution evaporated to crystallization. The crystals of cadmium nitrate were removed from the liquid, dissolved in pure water and recrystallized. The product obtained by the

[1] *Am. Chem. J.*, 14, 261.
[2] *Ztschr. anorg. Chem.*, 1, 364.

second recrystallization was dissolved in a little water and treated with a slight excess of potassium cyanide in a platinum dish. From this solution the metallic cadmium was thrown out by means of the electric current. The nitrate obtained by dissolving the electrolytic cadmium in pure nitric acid was tested spectroscopically and found to be free from impurities. The pure cadmium nitrate was digested with ammonium hydroxide and ammonium carbonate and the resulting cadmium carbonate ignited to oxide in a platinum crucible. The method of operation was very simple, a weighed portion of the oxide was dissolved in pure potassium cyanide, the solution electrolyzed and the resulting metallic cadmium weighed. The mean of nine observations computed on the basis of $O = 16$ gives 112.055 for the atomic mass of cadmium.

Bucher[1] made six series of experiments. The cadmium used was purified by nine distillations *in vacuo*. The weighings were all reduced to a vacuum standard and computed on the basis of $O = 16$, $S = 32.059$, $C = 12.003$, $Cl = 35.45$, $Br = 79.95$, and $Ag = 107.93$.

In the first series cadmium oxalate, dried for fifty hours at 150°, was ignited to oxide. The mean of eight observations gives 111.89 for the atomic mass of cadmium.

In the second series, cadmium oxalate was converted into sulphide by heating in a current of dry hydrogen sulphide. The mean of four determinations is $Cd = 112.15$.

In the third series a weighed quantity of cadmium chloride, dried at a temperature of 300° in hydrochloric acid gas, was precipitated with silver nitrate and the resulting silver chloride weighed. The mean of twenty-one determinations is $Cd = 112.39$. The separate observations in this series agree very closely.

The fourth series was similar to the third, except that cadmium bromide was used instead of the chloride. The mean of five determinations is $Cd = 112.38$, a result almost identical with that obtained from the chloride.

In the fifth series a weighed portion of metallic cadmium was converted into sulphate, which was dried at 400° and weighed.

[1] Thesis, Johns Hopkins University, *1894*.

The excess of sulphuric acid which remained with the sulphate was estimated and its weight deducted. The only result given is Cd = 112.35.

In the last series metallic cadmium was converted into oxide by dissolving in nitric acid and igniting the resulting cadmium nitrate. The mean of two determinations made by igniting the material in a porcelain crucible gives 112.08 for the atomic mass of cadmium. Three similar determinations made with a platinum crucible gave as a mean Cd = 111.87. From a series of experiments on cadmium oxide, Bucher concluded that a correction should be applied to the last and also the first series. By making this correction, the results in these two series would be very close to those obtained from the chloride and bromide.

From all the preceding determinations Clarke gives 111.93 as the most probable value for the atomic mass of cadmium. The large variation in the results of different experimenters has not been fully explained. Some chemists think that the larger values are due to a higher degree of purity in the metallic cadmium used, and hence regard these values as being more nearly correct. But it must be remembered that the reverse is true in the experiments of Dumas. From material which had not been purified, Dumas obtained results ranging from 112.32 to 112.76 for the atomic mass of cadmium, while from material which he considered absolutely pure, the results were from 111.76 to 112.13.

PREPARATION OF PURE CADMIUM.

The metallic cadmium used in these experiments was purified by distillation in a current of hydrogen which had been passed through solutions of caustic potash, lead nitrate, potassium permanganate, and sulphuric acid. A hard glass combustion tube was heated to redness and the walls of the tube indented at two points with a three-cornered file. This divided the tube into three parts. Commercial cadmium was placed in one end of the tube and connection made with the hydrogen generator. After complete removal of the air, the tube was carefully heated in a combustion furnace until one-half of the metal had distilled over into the middle portion of the tube. The metal was cooled in a

current of hydrogen. The tube was then broken and the meta removed. The portions in the first and last sections of the tub were rejected. The middle portion was placed in a second com bustion tube, similar to the first, and the distillation repeated After three distillations the metal was examined spectroscopically and found to be free from impurities.

FIRST SERIES.

EXPERIMENTS ON CADMIUM CHLORIDE.

Dumas and Bucher have both determined the ratio of cadmium to chlorine in cadmium chloride. The results given for the atomic mass of cadmium by the latter experimenter are almost four-tenths of a unit higher than those given by the former.

PREPARATION OF CADMIUM CHLORIDE.

Hydrochloric acid was purified by first passing chlorine through the commercial C. P. acid to remove any sulphur dioxide; the excess of chlorine was removed by a current of carbon dioxide. The acid was then distilled from calcium chloride and the hydrochloric acid gas collected in pure water. Pure metallic cadmium was then dissolved in the acid and the solution evaporated to crystallization. The crystals of cadmium chloride were removed from the liquid and thoroughly dried. The material was then placed in a hard glass combustion tube, similar to that used in the distillation of metallic cadmium, and carefully sublimed in a current of dry carbon dioxide. The first and last portions of the sublimate were rejected. The middle portion, which consisted of pearly leaflets, was placed in a weighing tube and kept in a desiccator. As only a small quantity of the material could be sublimed at a time, the different analyses were made from different sublimations.

MODE OF PROCEDURE.

A weighed portion of the cadmium chloride was dissolved in a little water in a platinum dish. A slight excess of potassium cyanide was added and, after diluting to 200 cc. with pure water, the solution was electrolyzed. Before interrupting the current, the liquid was siphoned from a dish in a manner already outlined

in the experiments on silver. The metallic deposit was washed several times with boiling water and carefully dried. The strength of the current and time of action were as follows:

Time of action.	Strength of current.
12 hours	$N.D_{100} = 0.1$ amperes.
4 "	$N.D_{100} = 0.15$ "
4 "	$N.D_{100} = 0.30$ "

The cadmium was thrown down as a dense white deposit.

Ten results on cadmium chloride reduced to a vacuum standard on the basis of:

3.3 = density of cadmium chloride,
8.55 = " " metallic cadmium,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $CdCl_2$, assuming 35.45 to be the atomic mass of chlorine, are as follows:

	Weight of $CdCl_2$. Grams.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.43140	0.26422	112.054
2	0.49165	0.30112	112.052
3	0.71752	0.43942	112.028
4	0.72188	0.44208	112.021
5	0.77264	0.47319	112.036
6	0.81224	0.49742	112.023
7	0.90022	0.55135	112.041
8	1.02072	0.62505	112.002
9	1.26322	0.77365	112.041
10	1.52344	0.93314	112.078

Mean = 112.038
Maximum = 112.078
Minimum = 112.002

Difference = 0.076
Probable error = ±0.005

From the total quantity of material used and metal obtained, we have 112.040 for the atomic mass of cadmium.

SECOND SERIES.

PREPARATION OF CADMIUM BROMIDE.

The bromine used in this series was purified as outlined in the experiments on mercuric bromide. The cadmium bromide was prepared by allowing bromine water to act on metallic cadmium for several days at the ordinary temperature. When the action

was complete, the solution was filtered and evaporated to crystallization. The crystals of cadmium bromide were removed from the liquid and thoroughly dried. The material was then placed in a hard glass combustion tube and carefully sublimed in a current of dry carbon dioxide. The first and last portions of the sublimate were rejected. The middle portion was removed from the tube, placed in a weighing bottle and kept in a desiccator. The product obtained in this way consisted of a crystalline, pearly leaflet which dissolved immediately in water without leaving a residue.

MODE OF PROCEDURE.

The method of operation was the same as for cadmium chloride. A weighed portion of the material was dissolved in a little water in a platinum dish. A slight excess of potassium cyanide was then added and after diluting to 200 cc. the solution was electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for cadmium chloride.

Ten observations on cadmium bromide reduced to a vacuum standard on a basis of:

4.8 = density of cadmium bromide,
8.55 = " " metallic cadmium,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $CdBr_2$, assuming 79.95 to be the atomic mass of bromine, are as follows:

	Weight of $CdBr_2$. Grams.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.57745	0.23790	112.031
2	0.76412	0.31484	112.052
3	0.91835	0.37842	112.067
4	1.01460	0.41808	112.068
5	1.15074	0.47414	112.053
6	1.24751	0.51392	112.019
7	1.25951	0.51905	112.087
8	1.51805	0.62556	112.076
9	1.63543	0.67378	112.034
10	2.15342	0.88722	112.041

Mean = 112.053
Maximum = 112.087
Minimum = 112.019

Difference = 0.068
Probable error = ±0.005

From the total quantity of material used and the metal obtained, Cd = 112.053.

THIRD SERIES.

In these experiments an attempt was made to determine the ratio of the atomic mass of cadmium to that of silver by allowing the same electric current to pass successively through solutions of the two metals and weighing the resulting deposits. The arrangement of apparatus and the details of the method were described under the mercury silver series. The results were not as satisfactory as the corresponding results obtained for mercury. A large number of determinations were made with currents of different strength and solutions of different concentration, but the results were, in most cases, far below those obtained in the first two series. A current which deposited about twelve hundredths of a gram of silver per hour seemed to give the best results. From all the observations, five results were selected which differed only about one-tenth of a unit from those of the first two series. Results selected in this way are entitled to but little weight, and perhaps should not be used in determining the general mean of all the observations.

Computed on the basis of 107.92 for the atomic mass of silver, the only admissible results are as follows:

	Weight of Ag. Gram.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.24335	0.12624	111.928
2	0.21262	0.11032	111.991
3	0.24515	0.12720	111.952
4	0.24331	0.12616	111.916
5	0.42520	0.22058	111.971

Mean = 111.952
Maximum = 111.991
Minimum = 111.916

Difference = 0.075

This method was discussed under mercury. The probable sources of error pointed out there apply equally well in the case of cadmium. Until the large variations can be accounted for

and the difficulties overcome, the method must be regarded as unsatisfactory.

SUMMARY.

Inasmuch as but one method of analysis has been used throughout this work, it is useless to discuss it here. The advantages and objections pointed out under silver apply also to cadmium.

In summing up the work on cadmium, equal weight must be given to the first two series. The last series must be considered alone and all that need be said of it is, that the results obtained for the atomic mass of cadmium never exceeded 112. In the corresponding series on mercury, the variations were in both directions from 200.

The general mean of the first two series calculated from the separate observations is:

	Atomic mass of Cd.
First series	= 112.038
Second series	= 112.053
General mean	= 112.0455

From the total quantity of material used and metal obtained we have:

	Atomic mass of Cd.
First series	= 112.040
Second series	= 112.053
General mean	= 112.0465

Combining this with the first general mean we have 112.046 as the most probable result of all the work, for the atomic mass of cadmium. This result is lower than those obtained by Huntington and Bucher, but agrees very closely with the results obtained by von Hauer, Dumas, Lensen, Jones, and Lorimer and Smith.

I wish here to express my sense of gratitude to Professor Edgar F. Smith, at whose suggestion this work was undertaken and under whose personal supervision it was carried out.

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Special Bulletin, Second Edition. Commercial Fertilizers. Purdue University, Lafayette, Indiana. August, 1896. 8 pp.

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Bulletin No. 127. Parasites of Domestic Animals. Issued by the North Carolina Agricultural Experiment Station, Raleigh, North Carolina. May 15, 1896. 42 pp.

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VOL. XVIII. [DECEMBER, 1896.] NO. 12.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. No. 14.]

METAL SEPARATIONS BY MEANS OF HYDROCHLORIC ACID GAS.[1]

BY J. BIRD MOYER.

Received September 26, 1896.

INTRODUCTION.

THE action of gaseous haloid acids upon metallic oxides and their salts, is a field of investigation, which, though not of recent origin, has been but lately developed. It was Debray[2] who first called attention to the volatility of molybdic acid in a stream of hydrochloric acid gas, with the formation of $MoO(OH)_2Cl_2$.

E. Péchard[3] applied this and showed that molybdic acid was completely eliminated and separated from tungstic acid, by its volatility in a current of hydrochloric acid. Since that time nothing further has been done with single haloid acids, in gas form, until quite recently. Compounds have been decomposed, salts volatilized, and separations made, by means of other gases and mixtures, which may be as effective as hydrochloric acid, but are not devoid of trouble nor nearly so neat.

Smith and Oberholtzer[4] repeated and confirmed Péchard's

1 From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Doctor of Philosophy, 1896.

2 *Compt. rend.*, 46 1098, and *Ann. Chem.* (Liebig), 108, 250.

3 *Compt. rend.*, 114, 173.

4 *J. Am. Chem. Soc.*, 15, 1.

work in regard to the separation of molybdic acid from tungstic acid, and in addition showed that gaseous hydrobromic, hydriodic, and hydrofluoric acids acted similarly. Later, Smith and Maas[1] made use of the volatilization of molybdic acid for a close atomic mass determination of molybdenum.

Smith and Hibbs[2] showed that vanadium behaved like molybdenum. Hydrochloric acid gas completely eliminates vanadic acid from sodium vanadate. A little later they investigated the action of hydrochloric acid upon the members of Group V of the periodic system.[3]

The sodium salts of nitric, pyrophosphoric, pyroarsenic and pyroantimonic acids were used. They found nitrogen, arsenic, and antimony to be volatile in gaseous hydrochloric acid, and made it the basis of a separation of phosphoric acid from nitric acid. Lead arsenate changed completely to chloride, the arsenic being volatilized, thus affording a good quick separation. Smith and Meyer[4] tried the action of all the haloid acids upon the elements of Group V of the periodic system. They worked with sodium salts and observed: I. That nitrogen was expelled completely by all the haloid acids. II. That phosphoric acid was not acted upon. III. That arsenic acid was fully expelled by hydrochloric, hydrobromic, and hydriodic acids, but only partially by hydrofluoric acid. IV. That antimony was completely volatilized by hydrochloric acid. There was no work done on bismuth. V. Vanadium went over completely in hydrochloric acid, but only partially in hydrobromic and hydrofluoric acids. VI. Columbium forms volatile products with hydrochloric and hydrobromic acids. No knowledge of didymium was obtained. VII. Tantalum is only slightly volatile in hydrochloric acid.

P. Jannasch and F. Schmidt[5] repeated some of the work of Smith and Hibbs, in which they confirmed the separation of arsenic from lead. They anticipated a slight portion of my work, and in addition separated arsenic acid from iron, tin from

[1] *Ztschr. anorg. Chem.*, 5, 280.
[2] *J. Am. Chem. Soc.*, 16, 578.
[3] *Ibid.*, 17, 682.
[4] *Ibid.*, 17, 735.
[5] *Ztschr. anorg. Chem.*, 9, 274.

lead, tin from copper, and tin from iron, in a stream of hydrochloric acid gas.

The position of bismuth in the periodic system makes it natural to suppose that it too will be volatile in hydrochloric acid gas. This I have shown to be true, and was thus enabled to separate it from lead and copper. The action of hydrobromic acid on bismuth trioxide was also tried; it formed the bromide and then volatilized. It requires a higher temperature and longer action than with hydrochloric acid. Because of lack of time, I have been compelled to abandon the experiments instituted with a view of affecting separations, in atmospheres of hydrobromic acid and hydriodic acid gas and have confined my labors to hydrochloric acid gas.

METHOD OF WORK.

The hydrochloric acid gas was generated by dropping concentrated sulphuric acid from a separatory funnel, upon concentrated hydrochloric acid contained in a three liter flask. The gas evolved at the ordinary temperature was dried by passing it through two sulphuric acid drying bottles and then through a calcium chloride tower, when it was considered sufficiently dry for the purpose. The substance to be acted upon was weighed out in a porcelain boat and the latter was placed in a combustion tube of hard glass.

The tube had previously been rinsed with alcohol and then with ether, to remove all moisture. The ether was removed by drawing a current of dry air through the tube. This tube was connected to a two-necked bulb receiver containing about 300 cc. of distilled water. When working with arsenic ten cc. of nitric acid were added. The connecting tube from the combustion tube to the bulb receiver was made to enter the receiver and dip below the surface of the water, thus catching all volatile products, as well as taking up the hydrochloric acid gas. To insure safety from the loss of volatile products, a small flask containing water was attached to the bulb receiver. The apparatus was controlled at both ends by stop-cocks. This is necessary to prevent backward suction on disconnecting the apparatus. After the reaction was completed the boat was removed to

a sulphuric acid desiccator from which the air could be exhausted. In general, the procedure was similar to that employed by Hibbs.[1]

I.—BEHAVIOR OF ANTIMONY TRIOXIDE.

Antimony oxide, labelled chemically pure, was dissolved in hydrochloric acid and precipitated with a large amount of water. After washing by decantation it was redissolved and reprecipitated. This procedure was repeated several times, when it was precipitated by ammonium carbonate, washed, and ignited. The pure oxide obtained in this manner was subjected to the action of hydrochloric acid gas and it was found to volatilize completely. In each trial a one-tenth gram of the oxide was acted upon. The temperature varied between 150° and 190° C. It was determined in the following way: The combustion tube was slipped through two holes made in the sides of a copper drying oven.

A very slow current of gas was used as the antimony seemed to volatilize more readily and completely, if the current was slow and the heat gentle. This I attribute, on reflection, to the fact that I ignited the oxide too strongly, (to a red heat) in its preparation. It dissolved with difficulty in concentrated hydrochloric acid. Lack of time prevented the repetition of this experiment and the separation of antimony from lead and copper, in which this substance was used. About eight hours was the time required for the volatilization; very probably a shorter time would be required if the oxide had been obtained by gentle ignition.

II.—BEHAVIOR OF LEAD OXIDE.

Pure lead oxide was obtained from recrystallized nitrate, by careful ignition. This oxide changed completely into chloride at the ordinary temperature and it was only necessary to apply a gentle heat to complete the change and entirely remove the water formed. No volatilization was noticed until a temperature of 225° was reached; at this point the lead chloride slightly volatilized.

I think it possible to estimate lead as chloride, if the temperature is kept under 200°. A weighed amount of lead oxide was

[1] Thesis, 1896.

acted upon by hydrochloric acid gas in the cold, for two hours, and then heated sufficiently to remove all the water formed.

The boat was cooled in the gas, and then placed in a sulphuric acid desiccator and allowed to stand one-half hour. It was then weighed.

EXPERIMENTS.

	Lead oxide taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.	Difference. Gram.
Experiment I	0.1017	0.1267	0.1267	0.0000
" II	0.1015	0.1258	0.1265	—0.0007
" III	0.1169	0.1454	0.1447	+0.0007

The lead chloride dissolved in hot water without residue.

III.—THE SEPARATION OF ANTIMONY FROM LEAD.

The oxides were carefully weighed and thoroughly mixed in a porcelain boat. Hydrochloric acid gas was passed over them in the cold, until the lead oxide had been entirely changed to the chloride. It was then heated with the smallest flame obtainable from a fish-tail burner, placed about two inches below the tube.

	Antimony trichloride taken. Gram.	Lead chloride taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.
Experiment I	0.1015	0.1189	0.1470	0.1482
" II	0.1090	0.1021	0.1266	0.1272
" III	0.1350	0.0852	0.1057	0.1062
" IV	0.1250	0.1671	0.2069	0.2083

The time required was seven hours. The lead chloride was immediately weighed. It dissolved completely in hot water and this solution was tested by means of Marsh's apparatus for antimony, without finding the latter present. Experiment II was slightly varied by first moistening the oxides with a drop of hydrochloric acid.

IV.—BEHAVIOR OF BISMUTH OXIDE.

Bismuth nitrate, as pure as could be obtained, was dissolved in nitric acid and then thrown down with a large quantity of water. The precipitate was carefully washed by decantation. This operation was repeated several times.

It was then dissolved in acidulated water and precipitated

with ammonium hydroxide and ammonium carbonate. This, on ignition, gave pure oxide, which, heated in a stream of hydrochloric acid gas, completely volatilized as chloride. Here the same treatment is necessary as obtained for antimony. A slow current of gas and a low heat were best adapted for the volatilization (a temperature of 130°, or roughly, the heat afforded by a fish-tail burner placed two inches below the combustion tube, with a flame an eighth of an inch high). The bismuth chloride sublimed nicely, forming a white crystalline mass beyond the boat, which could be readily driven along by a gentle heat.

V.—THE SEPARATION OF BISMUTH FROM LEAD.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed in a porcelain boat. Usually the gas was allowed to act in the cold for an hour, which changed the oxides completely to chlorides.

The same conditions prevailed as under bismuth oxide alone. If an attempt was made to hasten the reaction by heating higher than 180°, a little lead would volatilize. This sublimate, slightly yellow in color, would appear directly over the boat and could not be driven along the tube like bismuth, hence it was readily detected.

The separation of bismuth from lead requires much care, as it is not as sharp as could be desired. It is also difficult to tell exactly when the last traces of bismuth have been driven out of the boat, as there was no color change to indicate it, both metals forming white chlorides. The separation is complete in from six to seven hours. At the end of the separation the position of the boat was changed and the action continued; if no further sublimation occurred it was cooled and removed to a desiccator. The weight was taken after standing one-half hour over sulphuric acid. With care bismuth can be separated from lead in this manner.

	Lead oxide taken. Gram.	Bismuth trioxide taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.	Difference. Gram.
Experiment I	0.1014	0.2020	0.1261	0.1264	—0.0003
" II....	0.1006	0.0642	0.1252	0.1254	—0.0002
" III...	0.1038	0.1003	0.1294	0.1302	—0.0008
" IV ...	0.1412	0.1260	0.1759	0.1759	+0.0000

The chloride of lead dissolved completely in hot water. It showed no bismuth. The sublimate contained no lead.

VI.—BEHAVIOR OF CUPRIC OXIDE.

Pure copper nitrate was made by recrystallization. It was then ignited in a porcelain crucible at a dull red heat, until it became constant in weight. The pure black oxide was then subjected to the action of hydrochloric acid gas. In Experiment I, the boat containing the oxide was heated at the outset to 175°. It was taken out after two hours, placed over sulphuric acid for half an hour, and weighed. The weight showed that the copper oxide had hardly been acted upon. It had only been superficially changed to chloride. It was then moistened with two or three drops of hydrochloric acid, dried in a rapid current of the gas, and heated two hours longer. This resulted in the complete transformation into chloride. The anhydrous chloride thus obtained, liver brown in color, was placed in a desiccator from which the air was exhausted. This was done to remove all the gas that might be retained and prevented a too rapid absorption of moisture.

Copper chloride absorbs moisture but not so rapidly as to prevent weighing in this form :

	Copper oxide taken. Gram.	Copper chloride obtained. Gram.	Copper chloride required. Gram.	Difference. Gram.
Experiment I	0.1011	0.1708	0.1713	—0.0005
" II....	0.1025	0.1726	0.1736	—0.0010
" III...	0.1034	0.1756	0.1752	+0.0004

In Experiment II, the change was completed in the cold by prolonged action through four hours. It was then heated about ten minutes at the end to drive out the moisture that had formed. In all the experiments cited, the copper chloride, after weighing, was found to dissolve completely in cold water.

VII.—THE SEPARATION OF ANTIMONY FROM COPPER.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed. The antimony was completely volatilized, leaving copper chloride which was

weighed as such. The volatile antimony chloride was caught in the bulb receiver at the end of the tube. The bulb and tube were washed out with acidulated water into a beaker and the antimony thrown down with hydrogen sulphide. The antimony sulphide was filtered, thoroughly washed, and while moist dissolved in strong hydrochloric acid. The hydrogen sulphide evolved was conducted into bromine water and oxidized to sulphuric acid, which was estimated as usual and the antimony calculated.

The length of time required was eight hours. On several occasions the experiment was interrupted at the end of four hours, but invariably the separation was incomplete and on dissolving out the copper chloride formed, black copper oxide and white antimony oxide were plainly evident. In some cases the mixture of oxides was moistened with a couple of drops of hydrochloric acid and then evaporated down in a stream of acid gas, by heating the tube over a water-bath. This treatment seemed to facilitate matters but it is not altogether advisable, because the copper chloride has a tendency to creep over the sides of the boat. It is quicker in the end to separate them in the dry condition, allowing plenty of time for the reaction. The copper chloride obtained was perfectly soluble in cold water and contained no antimony. It could readily be changed to oxide and weighed if thought necessary.

	Antimony trioxide taken. Gram.	Copper oxide taken. Gram.	Copper chloride obtained. Gram.	Copper chloride required. Gram.	Difference. Gram.
Experiment I	0.1068	0.1040	0.1750	0.1745	+0.0005
" II	0.1062	0.1053	0.1774	0.1784	—0.0010
" III	0.1022	0.1020	0.1726	0.1728	—0.0002
" IV	0.1198	0.1020	0.1722	0.1728	—0.0006

	Antimony trioxide taken. Gram.	Antimony trioxide found. Gram.	Difference. Gram.
Experiment I	0.1068	0.1059	+0.0009

VIII.—THE SEPARATION OF BISMUTH FROM COPPER.

The pure oxides were mixed and treated as directed under bismuth and lead.

	Copper oxide taken.	Bismuth trichloride taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Gram.	Grams.	Grams.	Grams.	Grams.
Experiment I ..	0.1030	0.1069	0.1738	0.1745	—0.0007
" II..	0.1004	0.1077	0.1701	0.1713	—0.0012
" III.	0.1026	0.1060	0.1741	0.1738	+0.0003
" IV.	0.1019	0.1058	0.1718	0.1726	—0.0008

	Bismuth trioxide obtained.	Bismuth trioxide required.	Difference
	Gram.	Gram.	Gram.
Experiment I..............	0.1076	0.1069	+0.0007

The time required in each of these trials was seven hours. It seemed to be advantageous to raise the temperature and heat sharply for about ten minutes at the end, to insure the complete removal of the bismuth.

Moistening with acid helped the reaction but subjected it to the same danger of creeping as noted under antimony and copper.

The bismuth was estimated as follows: It was washed out of the tube and bulb with acidulated water and then precipitated as sulphide. The bismuth sulphide was filtered, washed, and dissolved in nitric acid. It was thrown out of the solution with ammonium hydroxide and ammonium carbonate, as hydrated oxide, and then filtered, dried, and ignited. It was weighed as oxide. The residue of copper chloride in the boat dissolved in cold water and showed no bismuth.

IX.—ACTION OF GASEOUS HYDROCHLORIC ACID ON SODIUM PYROARSENATE.

Hibbs[1] showed that arsenic was completely volatilized from sodium pyroarsenate, leaving weighable sodium chloride. In fact, so clean was the elimination of arsenic that he made it the basis of an arsenic atomic mass determination, with admirable success.

In working up the separation of arsenic from other metals it was necessary to start with the pure sodium salt. After purification I decided to test it, by weighing the salt produced by the action of the acid gas upon it. Several determinations gave close results, proving the salt pure.

[1] See next paper, page 1044.

Chemically pure arsenate was procured. It was recrystallized and then ignited (not too strongly) for an hour. The pyroarsenate obtained was used in precipitating the various arsenates investigated.

	Sodium pyroarsenate taken. Gram.	Sodium chloride obtained. Gram.	Sodium chloride required. Gram.
Experiment I	0.2021	0.1330	0.1335
" II	0.1039	0.0691	0.0686

X.—THE SEPARATION OF ARSENIC FROM COPPER.

Pure sodium pyroarsenate was used to precipitate the copper salt.

Copper sulphate was recrystallized five times, a few good crystals were dissolved and the two solutions mixed. A green copper arsenate was precipitated. It was washed and dried at 100°. Salkowski[1] observes that copper arsenate still contains water above 130°. My salt had the composition $Cu_2As_2O_8 +$ $2H_2O$.

Hydrochloric acid gas completely changes it in the cold to chloride. A slight heat drives out the arsenic and water and leaves a brown anhydrous copper chloride, which can be weighed as such. Care was taken to remove all the acid gas before weighing.

The arsenic was washed out of the bulb into a beaker, this was warmed with nitric acid to insure oxidation, and then it was precipitated from an ammoniacal solution with "a magnesia mixture." It was weighed as $Mg_2As_2O_7$.

	Copper arsenate taken. Gram.	Copper chloride obtained. Gram.	Copper chloride required. Gram.	Difference. Gram.
Experiment I	0.1067	0.0850	0.0851	—0.0001
" II	0.1240	0.0998	0.0991	+0.0007
" III	0.1072	0.0860	0.0856	+0.0004
" IV	0.1155	0.0924	0.0923	+0.0001
" V	0.1042	0.0832	0.0833	—0.0001

Experiment I. As_2O_5 obtained, 0.0498 gram; As_2O_5 required, 0.0487 gram.

The residue of copper chloride completely dissolved in water. It showed no arsenic when tested in a Marsh apparatus.

[1] *J. prakt. Chem.*, 104, 129.

XI.—THE SEPARATION OF ARSENIC FROM SILVER.

Silver arsenate was made by precipitating silver nitrate with sodium arsenate. Care was taken to have the nitrate in excess. The reddish-brown arsenate of silver was washed with boiling water, until the washings no longer showed silver, when tested with hydrochloric acid. It was dried at 110°.

As was expected, the acid gas attacked it even in the cold. In fact the action was so vigorous that a couple of analyses were spoiled by spattering. The trouble arose from the fact that the arsenate was not finely powdered. Heat was generated in the reaction sufficiently to send over a portion of the water formed. Experiment I was run in the cold for one hour and then heated sharply, for a few minutes, to expel the arsenic and water. The result was only 0.46 per cent. too high, but indicated that the salt should be heated longer, and not necessarily as high to remove all the arsenic.

The succeeding experiments were heated from one to two hours at 150° with better results:

	Silver arsenate taken. Gram.	Silver chloride obtained. Gram.	Silver chloride required. Gram.	Difference. Gram.
Experiment I.....	0.2542	0.2381	0.2363	+0.0018
" II....	0.2325	0.2163	0.2161	+0.0002
" III...	0.2084	0.1952	0.1938	+0.0014
" IV...	0.2070	0.1927	0.1924	+0.0003

Experiment I. Ag obtained = 70.45 per cent; Ag required = 69.99 per cent.

The residues in Experiments II, III, and IV were dissolved and tested for arsenic. None was found.

XII.—THE SEPARATION OF ARSENIC FROM CADMIUM.

Chemically pure cadmium sulphate was precipitated by a solution of sodium pyroarsenate. Stirring brought out a gelatinous arsenate, which changed by additional stirring to a granular salt. This was thoroughly washed and dried at 110°. It had the composition $Cd_2As_2O_7 + 2H_2O$. Salkowski[1] observes that a red heat is necessary to fully dehydrate this salt.

The moisture and arsenic were completely expelled at 150°,

[1] *Loc. cit.*

leaving a uniform mass of cadmium chloride. It was weighed as such after standing over sulphuric acid for one-half hour. The arsenic was determined as usual.

	$Cd_3As_2O_8 + 2H_2O$ taken. Gram.	Cadmium chloride obtained. Gram.	Cadmium chloride required. Gram.	Difference. Gram.
Experiment I	0.2359	0.1965	0.1977	−0.0012
" II ...	0.1166	0.0968	0.0968	−0.0000
" III...	0.1030	0.0857	0.0855	+0.0002
" IV ...	0.1138	0.0947	0.0946	+0.0001
" V	0.1043	0.0870	0.0867	+0.0003
	$Cd_3As_2O_8 + 2H_2O$ taken. Gram.	As_2O_5 obtained. Gram.	As_2O_5 required. Gram.	Difference. Gram.
Experiment I	0.2359	0.0813	0.0822	0.0009

The cadmium chloride dissolved perfectly in water and showed no arsenic, when tested in a Marsh apparatus.

XIII.—THE ACTION OF HYDROCHLORIC ACID GAS ON FERRIC OXIDE.

Pure oxide of iron was heated in a stream of acid gas. The behavior of iron is rather peculiar, as it very readily changes into chloride, and then only partially volatilizes. On heating to 200° the greater part is driven over as flaky crystals of ferric chloride. The remainder consists of a white mass, which refuses to go over on prolonged action and also on raising the temperature.

This residue was soluble in water and did not react with potassium thiocyanate, but immediately gave a blue precipitate with ferricyanide. Reduction was therefore evident; this is also noted by Jannasch and Schmidt.[1] The temperature at which ferric chloride usually goes into the ferrous condition is above 1000°.

Care was taken to prepare perfectly pure hydrochloric acid gas. Chemically pure acids were used to this end. The action however was the same in all cases.

XIV.—THE SEPARATION OF ARSENIC FROM IRON.

Chemically pure ferrous ammonium sulphate was carefully

[1] *Loc. cit.*

oxidized with nitric acid, it was taken up in water, filtered and then crystallized several times. The best crystals were selected and a solution made to precipitate the arsenate. A white precipitate tinged with yellow was formed. It was washed by decantation and then filtered and washed until the washings no longer gave Prussian blue with ferrocyanide. It was then dried and gently ignited.

The acid gas acts on it quickly in the cold and it becomes a light green liquid. In evaporating off the moisture the chloride of iron was carried over with the arsenic.

In a second trial, with the temperature lower and occasionally removing the source of the heat altogether, when ebullition threatened to cause spattering, ferric chloride was obtained without loss. This was gradually heated a little higher to remove all the arsenic.

The chloride of iron was dissolved, oxidized, precipitated with ammonium hydroxide and estimated as usual. The result was fair and the product tested showed the absence of arsenic, but all succeeding experiments failed. Either the substance spattered or the iron went along with the arsenic.

Jannasch and Schmidt[1] separated arsenic from iron by placing their material in a large hard glass bulb and evaporating down to dryness with nitric acid, in an air current. This is not applicable when a porcelain boat is employed. They then volatilized the arsenic in hydrochloric acid gas at 120°.

XV.—SEPARATION OF ARSENIC FROM ZINC.

In some preliminary work zinc oxide was treated with acid gas at 200°. It completely changed to chloride and was not volatile. Pure zinc sulphate was used to precipitate the arsenate; it was washed, dried and ignited to 150°. The same difficulty appeared as was encountered under iron. Zinc arsenate melts down to a liquid mass as soon as the acid gas strikes it, which is extremely hard to evaporate without spattering. A small glass cover was placed over the boat, which tended to lessen the spattering, but did not entirely prevent it.

The zinc was estimated by taking the chloride up in a little

[1] *Loc. cit.*

hydrochloric acid and running it down with pure mercuric oxide. It was then ignited and weighed as zinc oxide. One good result was obtained, but generally the residues of zinc contained arsenic and the results were far from being concordant.

XVI.—THE SEPARATION OF ARSENIC FROM COBALT AND NICKEL.

Cobalt and nickel were precipitated as arsenates in the usual manner, with a solution of pyroarsenate.

Cobalt nitrate, a Merck preparation, was carefully purified; considerable manganese was found and eliminated.

This gave the pink salt $Co_3As_2O_8 + 8H_2O$, which was ignited to the blue anhydrous compound.

Cobalt arsenate is very readily attacked by the acid gas in the cold, yielding a pink chloride. A slight heat, not much above 120°, changed it to the blue chloride and drove out the arsenic. At first it was quickly weighed as chloride, then it was taken up in a little hydrochloric acid and evaporated down with mercuric oxide. On ignition, black Co_3O_4 was obtained and weighed.

The arsenic was estimated as usual.

	Experiment I. Gram.	Experiment II. Gram.
$Co_3As_2O_8$ taken	0.1509	0.2029
$CoCl_2$ obtained	0.1309	....
$CoCl_2$ required	0.1293	....
Co_3O_4 obtained	0.0738	0.0969
Co_3O_4 required	0.0731	0.0983
Difference	+0.0007	—0.0014
As_2O_5 obtained	0.0770	....
As_2O_5 required	0.0764	....
Difference	+0.0006	....

On testing the cobalt residue by the Marsh test, no trace of arsenic was found. No cobalt was found in the sublimate. Some of the first experiments gave cobalt too low; it was thought that they had been heated too high, but testing showed no volatilized cobalt.

A temperature of 125° is sufficient to drive out all of the arsenic, and at this temperature there is no danger of volatilizing the cobalt.

In working with nickel, the green arsenate was simply dried

in the first experiment. It therefore had the composition $Ni_3As_2O_8 + 8H_2O$.

Hydrochloric acid gas attacked it in the cold. A slight heat drives out the arsenic and moisture and leaves a salmon-colored chloride. The nickel chloride was changed to oxide by evaporating it with nitric acid and igniting.

	Experiment I. Gram.
$Ni_3As_2O_8 + 8H_2O$ taken	0.1502
NiO obtained	0.0554
NiO required	0.0561
Difference	—0.0007

In Experiments II and III the salt was made anhydrous by ignition.

	Experiment II. Gram.	Experiment III. Gram.
$Ni_3As_2O_8$ taken	0.1166	0.1040
NiO obtained	0.0577	0.0523
NiO required	0.0575	0.0513
Difference	+0.0002	+0.0010
As_2O_5 obtained	....	0.0515
As_2O_5 required	....	0.0526
Difference	....	—0.0011

The Marsh test showed no arsenic with the nickel.

XVII.—BEHAVIOR OF MINERALS IN HYDROCHLORIC ACID GAS.

Niccolite. One-half gram of the mineral was finely powdered and subjected to the action of acid gas for a day, at a temperature of 200° C. It was only very slightly affected.

A second portion was dissolved in nitric acid and evaporated down in a porcelain dish. It was then transferred to a boat and evaporated to dryness. To remove all the acid, it was heated in an oven to 110° for one-half hour. The dry substance was acted upon by the acid gas in the cold for five hours. It changed completely to chloride. A temperature of 150° for an hour removed all the moisture and arsenic.

The nickel chloride was evaporated down with nitric acid, ignited, and weighed as NiO. The arsenic was estimated as usual.

	Per cent.
Nickel found	43.79
Nickel calculated	43.60
Difference	0.19
Arsenic found	56.66
Arsenic calculated	56.40
Difference	0.26

Undoubtedly there is still a wide field open in regard to the behavior of hydrochloric acid gas upon mineral species. Smith and Hibbs[1] showed that mimetite lost its arsenic quantitatively, when heated in a stream of acid gas. In this laboratory others are being investigated with favorable indications. The direct employment of hydrochloric acid gas upon a powdered mineral would simplify many a tedious gravimetric process, leaving the separated elements in a desirable condition for further treatment.

In the case of a mineral such as niccolite, where it must first be decomposed with nitric acid and then transferred to a boat, the advantage is not so great. This, however, can be modified, so that the time factor is reduced and the advantage of the method still retained. Instead of using a boat, which has no advantage unless the non-volatile chlorides are to be weighed directly, a hard glass bulb can be substituted. The mineral is placed in the bulb, dissolved in nitric acid, and evaporated down by the aid of a current of air drawn through the bulb.

The residual oxides are then separated in a stream of hydrochloric acid gas as usual.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 15.]

THE ATOMIC WEIGHTS OF NITROGEN AND ARSENIC.[2]

BY JOSEPH GILLINGHAM HIBBS.

Received September 26, 1896.

THE atomic weight of the metal molybdenum had been determined by expelling molybdic acid from sodium molybdate with hydrochloric acid gas, then weighing the residual sodium chloride.

1 *Loc. cit.*

2 From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Doctor of Philosophy, 1896.

Having found that nitric acid and arsenic acid were driven from their alkali salts with ease, leaving a chloride that was absolutely pure, and believing that the atomic masses of nitrogen and arsenic determined in this manner would afford a valuable contribution to the literature relating to these constants, a carefully conducted series of experiments was made with two nitrates and one arsenate. The results are given in detail in the following lines :

THE ATOMIC WEIGHT OF NITROGEN.

In the past, determinations of the atomic weight of nitrogen have been made from the density of the gas itself, from the ratio between ammonium chloride and silver, and from the decomposition of certain nitrates. The first method in particular has been frequently applied. Thomson, Dulong, Berzelius, and Lavoisier brought to light many new facts relating to the atomic weight of nitrogen; unfortunately, however, considerable that they have presented has been affected by complications that have introduced inaccuracies.

Dumas and Boussingault[1] found the mean density of nitrogen to be 0.972 ; for hydrogen they found a mean density of 0.0693, which would give nitrogen an atomic weight of 14.026. Regnault obtained a more concordant series of results, the mean being 0.97137, and a density for hydrogen of 0.0692, which makes the atomic weight of nitrogen equal to 14.0244.

Clarke gives in detail his computation of the means of the results obtained by Penny, Stas, and Marignac. Their work on the determination of the atomic weight of this particular element was mainly on the ratio of ammonium chloride and silver, and the decomposition of certain nitrates. A great degree of accuracy was maintained throughout the entire investigation ; but the amount of work required to obtain a single result necessarily lays the method open to a serious error of manipulation.

In this connection a paragraph from Clarke's "A Recalculation of the Atomic Weights" may be cited : "The general method of working upon these ratios is due to Penny. Applied to the ratio between the chloride and nitrate of potassium, it is

[1] *Compt. rend.*, 1841—12. 1005.

as follows: A weighed quantity of the chloride is introduced into a flask which is placed upon its side and connected with a receiver. An excess of pure nitric acid is added, and the transformation is gradually brought about by the aid of heat, the nitrate being brought into a weighable form. The liquid in the receiver is also evaporated, and the trace of solid matter which has been mechanically carried over, is recovered and also taken into account."

The method indicated in this study, and actually applied with the results appended, is decidedly less objectionable. In this method there is no distillation, no precipitate, in fact, nothing that could involve serious error.

Clarke summarizes the results of Penny, Stas, and Marignac as follows:

1.	From specific gravity of N	N = 14.0244
2.	" ammonium chloride	N = 14.0336
3.	" ratio number four	N = 14.0330
4.	" silver nitrate	N = 13.9840
5.	" potassium nitrate	N = 13.9774
6.	" sodium nitrate	N = 13.9906
	Mean of results for N	N = 14.0210

If oxygen is 16, this becomes 14.0291. Stas found the atomic weight of nitrogen to be 14.044. Dumas found 14 by experiments on the combustion of ammonia and cyanogen ($O = 16$). Pelouze found 14.014 by bringing a known weight of silver nitrate in contact with a known and slightly excessive weight of ammonium chloride, which excess was titrated. Anderson found 13.95 by the decomposition of the nitrate of lead, with just enough heat for decomposition (the same method that was used by Berzelius). Marignac found 14.02 by dissolving a known weight of silver in nitric acid and then melting and weighing the nitrate found.

A.—ATOMIC WEIGHT OF NITROGEN BY ACTION OF HYDROGEN CHLORIDE UPON POTASSIUM NITRATE.

The purest salt obtainable was dissolved in water, filtered, and recrystallized six times, a solution of which was tested for chlorides, sulphates, etc., but no impurity was found. One more crystallization was made and the best crystals were

selected. These were washed with distilled water and dried at 210° C. for three hours, powdered, and again dried, and finally placed in a weighing bottle. This compound was dried before each experiment. It was also allowed to stand in a balance case one hour before weighing. The same degree of care was exercised in the preparation of the boat for weighing.

The weighing bottle was placed on the scale pan and allowed to stand several minutes in order to regain its normal temperature. After weighing it was quickly opened and a portion of the salt removed to the boat and again closed and allowed to stand in the balance case for several hours before reweighing. The boat was then introduced into the combustion tube and the gas passed over it. The characteristic action took place. The only difference in the method of procedure adopted here and that described in the first section of this paper, was a longer time being given to complete the action, using a lower temperature, in order to do away with all possibility of fusion of the salt. It was then carefully removed to a vacuum desiccator and allowed to stand over night before weighing. It may be said also that experiments were only conducted on clear days to insure the non-entrance of moisture.

With potassium nitrate, no great variation of amount was taken.

Five determinations were made in this case :

No.	Potassium nitrate taken. Gram.	Potassium chloride obtained. Gram.	Correction for potassium nitrate. Gram.	Correction for potassium chloride. Gram.	Correction for weight of potassium nitrate Gram.	Correction for weight of potassium chloride. Gram.	Molecular weight of potassium nitrate obtained.	Atomic weight of nitrogen obtained.
1.	0.11084	0.08173	0.00006	0.00004	0.11090	0.08177	0.101121	14.011
2.	0.14864	0.00960	0.00007	0.00005	0.14871	0.10965	0.101120	14.010
3.	0.21056	0.15525	0.00011	0.00008	0.21067	0.15533	0.101123	14.013
4.	0.23248	0.17214	0.00012	0.00009	0.23360	0.17223	0.101121	14.011
5.	0.24271	0.17894	0.00013	0.00009	0.24284	0.17903	0.101124	14.014

Atomic weight of nitrogen $= 14.0118 \pm 0.000472$.

The atomic values used in these calculations were taken from "Table of Atomic Masses," revised by F. W. Clarke, in October, 1891.

The figures deduced from these values are, of course, subject to any change made by later revision of atomic weights. It is not so much the exact figure to which attention is called, as to the constancy of result brought forward by this method. The values used were:

Oxygen	16.00
Potassium	39.11
Chlorine	35.45
Specific gravity potassium nitrate	2.1
Specific gravity potassium chloride	1.99

B.—ATOMIC WEIGHT OF NITROGEN BY ACTION OF HYDROGEN CHLORIDE UPON SODIUM NITRATE.

The same degree of care and method of procedure were here observed as in Division A. The results are as follows:

No.	Potassium nitrate taken. Gram.	Sodium chloride obtained. Gram.	Correction for sodium nitrate. Gram.	Correction for sodium chloride. Gram.	Correction for sodium nitrate. Gram.	Correction for sodium chloride. Gram.	Molecular weight of sodium nitrate.	Atomic weight of nitrogen.
1.	0.01550	0.01064	....	....	0.01550	0.01066	85.061	14.011
2.	0.20967	0.14419	0.00009	0.00007	0.20976	0.14426	85.061	14.011
3.	6.26217	0.18029	0.00012	0.00009	0.26229	0.18038	85.064	14.014
4.	0.66610	0.46805	0.00035	0.00024	0.66645	0.45829	85.064	14.014
5.	0.93676	0.64422	0.00042	0.00034	0.93718	0.64456	85.058	14.008

Atomic weight of nitrogen $= 14.0116 \pm 0.000741$.

Atomic values used were

Oxygen	16.00
Sodium	23.05
Chlorine	35.45
Specific gravity sodium chloride	2.16
Specific gravity sodium nitrate	2.26

When these results are compared with those obtained by Penny and Stas by treatment of potassium chloride with nitric acid, and the treatment of potassium nitrate with hydrochloric acid (likewise for sodium), a close comparison can be made.

Penny.		Hydrogen chloride method.	
For potassium nitrate	13.9774	For potassium nitrate	14.0118
" sodium nitrate	13.9906	" sodium nitrate	14.0116

Showing a difference of

0.0344 for potassium salt,
0.0210 for sodium salt.

When a mean of the above results is taken, the atomic weight of nitrogen equals

13.9996 for potassium salt,
14.0011 for sodium salt.

Taking now a mean of these values, the atomic weight of nitrogen would be 14.0003.

C.—THE ATOMIC WEIGHT OF ARSENIC.

The atomic weight of arsenic has been obtained from the chloride ($AsCl_3$), the bromide ($AsBr_3$), and the trioxide (As_2O_3).

Pelouze, in 1845,[1] and Dumas, in 1859, determined it by the titration with known quantities of pure silver in the analysis of arsenic trichloride. The mean of their results, as computed by Clarke, gives the atomic weight of arsenic, 74.829. Wallace[2] makes the same titration with silver in the analysis of arsenic tribromide. His value is 74.046. Kessler made a set of determinations by estimating the amount of potassium bichromate required to oxidize 100 parts of arsenic trioxide to arsenic pentoxide. He obtained a mean value of 75.002.

A mean of these results gives the following:

From $AsCl_3$	74 829
" $AsBr_3$	74.046
" As_2O_3	75.002
General mean	74.918

If oxygen = 16, then the atomic weight of arsenic will equal 75.090.

Berzelius, in 1826, heated sulphur and arsenic trioxide together in such a way that sulphur dioxide alone escaped; this method gave 74.840 as the atomic weight of arsenic. But one experiment was made, so that it does not possess much value. In the above method there seems to be a wide variation in the results obtained, the difference between the extreme values is but little less than one unit.

By the hydrogen chloride method, we have but the weighing of the material used in the determination—which must necessarily enter every estimation or analysis—and a single weighing after the action of the acid gas. As in the case of nitrogen, the method seems to be as short and concise as possible.

1 *Compt. rend.*, 10, 1047.
2 Phil. Mag. (4), 18, 279.

The methods and *modus operandi* were exactly the same as those used in the determination of the atomic weight of nitrogen.

The sodium chloride obtained was perfectly white in color. In no instance was it fused. After weighing the salt residue it showed no traces of arsenic, and was readily soluble in cold water without residue. The same conditions of atmosphere were observed.

As the specific gravity of sodium pyroarsenate could not be obtained, it was determined by means of the specific gravity bottle, against chloroform, and was found to be 2.205, while the specific gravity of sodium chloride was taken as 2.16. The atomic values used were:

Oxygen	16.00
Sodium	23.05
Chlorine	35.45

The results here obtained, besides being to a great degree constant, compare favorably with those obtained by Pelouze (74.829) and Kessler (75.002).

A coincidence may here be shown by the fact that the mean of these values gives 74.9155, while the hydrogen chloride method gives 74.9158.

In order to give the method a thorough trial, the amounts taken cover a wide range. The smallest amount used was 0.02176 gram of sodium pyroarsenate, and the largest 3.22485 grams. It will also be noticed that the variation in result is but 0.027 for ten determinations.

No.	Sodium pyroarsenate taken. Gram.	Sodium chloride obtained. Gram.	Correction for sodium pyroarsenate. Gram.	Correction for sodium chloride. Gram.	Correction for sodium pyroarsenate. Gram.	Correction for sodium chloride. Gram.	Molecular weight of sodium pyroarsenate.	Atomic weight of arsenic.
1.	0.02176	0.01439	0.00001	0.00000	0.02177	0.01439	354.008	74.904
2.	0.04711	0.03114	0.00002	0.00001	0.04713	0.03115	354.042	74.921
3.	0.05792	0.03828	0.00003	0.00002	0.05795	0.03830	354.054	74.927
4.	0.40780	0.26970	0.00021	0.00011	0.40801	0.26981	354.002	74.901
5.	0.50440	0.33028	0.00026	0.00017	0.50466	0.33045	354.033	74.916
6.	0.77497	0.51222	0.00041	0.00027	0.77538	0.51249	354.034	74.917
7.	0.82853	0.54762	0.00044	0.00029	0.82897	0.54791	354.034	74.917
8.	1.19068	0.78690	0.00056	0.00041	1.19124	0.78731	354.053	74.926
9.	1.67464	1.10681	0.00081	0.00051	1.67545	1.10732	354.057	74.928
10.	3.22485	2.13168	0.00152	0.00099	3.22637	2.13267	354.002	74.901

Atomic weight of arsenic = 74.9158 ± 0.00222.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No 16.]

THE SEPARATION OF VANADIUM FROM ARSENIC.

BY CHARLES FIELD, 3RD, AND EDGAR F. SMITH.

Received October 2, 1896.

AS vanadium and arsenic occur associated in minerals and likewise in artificial products, their separation becomes a matter of consequence.

The course usually pursued in carrying out this separation is that long since recommended for the removal of vanadic acid from its solutions; namely, its precipitation as ammonium metavanadate. Other methods have recently appeared in the literature bearing on analysis. Reference is here made especially to the publication of Fischer.[1]

Experiments made in this laboratory on the behavior of vanadates[2] and arsenates[3] heated in an atmosphere of hydrochloric acid gas, in which both acids were volatilized, suggested the thought that if the sulphides of vanadium and arsenic were exposed to the same vapors perhaps they would show a variation in deportment. And so it has proved. Perfectly dry arsenic trisulphide, previously washed with alcohol, carbon disulphide, and ether, then dried at 100° C., when exposed in a porcelain boat, placed in a combustion tube, was almost completely expelled from the retaining vessel at the ordinary temperature. The last traces were driven out at a temperature little above 150° C. Brown vanadium sulphide, in a perfectly dry condition, treated in the same manner, was not altered. It only remained then to prepare mixtures of known amounts of the two sulphides and subject them to the action of the acid vapor. To this end the following experiments were made:

I. 0.1303 gram of vanadium sulphide,
0.1302 gram of arsenic sulphide.

The arsenic sulphide was volatilized without difficulty and left 0.1297 gram of vanadium sulphide.

1 Bestimmung von Vanadinsäure: Dissertation, Rostock, 1894.
2 *J. Am. Chem. Soc.*, 16, 578.
3 *Ibid.*, 17, 682.

II. 0.1290 gram of vanadium sulphide,
0.2242 gram of arsenic sulphide,

gave after exposure of one hour to hydrochloric acid vapor a residue of vanadium sulphide, weighing 0.1297 gram.

III. 0.0828 gram of vanadium sulphide,
0.0582 gram of arsenic sulphide,

left 0.0827 gram of vanadium sulphide.

IV. 0.1306 gram of vanadium sulphide,
0.2028 gram of arsenic sulphide,

gave a residue of 0.1308 gram of vanadium sulphide.

V. 0.1403 gram of vanadium sulphide,
0.2409 gram of arsenic sulphide,

left 0.1404 gram of vanadium sulphide.

The temperature in these experiments was not allowed to exceed 250° C., as beyond that point there is danger of affecting the vanadium and causing its partial volatilization.

The method worked so well and with such evidently favorable results that the following course was adopted in the analysis of a specimen of the mineral vanadinite. 0.2500 gram of air-dried and finely divided material was placed in a porcelain boat; the latter was then introduced into a combustion tube and gently heated in a current of dry hydrochloric acid gas. By this treatment vanadic and arsenic oxides were expelled, leaving lead phosphate and chloride. The receiver containing the vanadium and arsenic was made alkaline and digested with ammonium sulphide. From the solution of the sulpho-salts the vanadium and arsenic sulphides were set free by a dilute acid. After washing and careful drying these sulphides were separated as indicated in the preceding lines, then changed to oxides and determined in the usual manner. The sum of the total constituents determined as lead oxide, phosphoric oxide, vanadic and arsenic oxides, with some lead chloride, amounted to 0.2501 gram.

The method in addition to being satisfactory in the analytical way, certainly forms a very excellent means of purifying and freeing vanadium from arsenic.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 17.]

THE SEPARATION OF MANGANESE FROM TUNGSTIC ACID.

BY WALTER T. TAGGART AND EDGAR F. SMITH.

Received October 2, 1896.

THE necessity of obtaining pure tungstic acid from time to time, using wolframite as the starting out material, has frequently suggested the inquiry as to what course would probably prove the best in the quantitative separation of this acid from oxides, such as those of iron and manganese.

In the experiments recorded in this communication only the results obtained from a study of mixtures of a manganous salt and a soluble alkali tungstate will be given. The directions taken in the experimentation were, 1st, to effect the separation by the use of yellow ammonium sulphide in the presence of ammonium chloride; 2nd, to eliminate the acid oxide by the use of an alkaline carbonate.

Following the first course, mixtures of definite amounts of ammonium tungstate and manganous chloride were made. To these was added water and a considerable excess of yellow ammonium sulphide, together with ammonium chloride. The mixtures were digested on a water-bath at 70° C., for several hours, and the vessels containing them were then closed and allowed to stand during the night. The manganese sulphide was filtered out, and, after solution, was changed into sulphate and weighed as such, or it was finally obtained as protosesquioxide in the customary way.

RESULTS.

Manganous oxide present. Gram.	Manganous oxide found. Gram.
0.1950	0.2121
0.1949	0.2255
0.1290	0.1708
0.1287	0.1720
0.1291	0.1760

In every trial tungstic acid adhered to the metallic oxide.

In trying the second suggestion the soluble tungstate and the

soluble manganous salt were digested for some hours in a platinum dish, upon a water-bath, with an excess of a ten per cent. potassium carbonate solution, after which the whole was evaporated to dryness, the residue boiled up with water, the manganous carbonate filtered out, washed, and finally converted into protosesquioxide.

RESULTS.

Manganous oxide present. Gram.	Manganous oxide found. Gram.
0.1949	0.1516
0.1949	0.1534

Several trial were made using a fifty per cent. solution of potassium carbonate.

RESULTS.

Manganous oxide present. Gram.	Manganous oxide found. Gram.
0.1951	0.1745
0.1950	0.1528

The experimental evidence given in the preceding paragraphs leaves no doubt as to the insufficiency of the two methods, which were tried, in effecting the desired separation. It is probable that fusion with an alkaline carbonate will alone answer for this purpose. How complete that course would be can only be ascertained by careful experimentation.

In the course of analysis molybdenum is quite often obtained as sulphide. Its conversion into a weighable form is attended with more or less difficulty. Trials made in connection with its estimation show that if the sulphide, as generally obtained, be dried, then intimately mixed with anhydrous oxalic acid, its careful ignition to trioxide can be made quite rapidly.

RESULTS.

Molybdenum trioxide taken. Gram.	Molybdenum trioxide found. Gram.
0.3000	0.3009
0.3000	0.2990
0.1007	0.1011

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 18.]

THE SEPARATION OF BISMUTH FROM LEAD.

BY ARTHUR L. BENKERT AND EDGAR F. SMITH.

Received October 2, 1896.

MANY methods have been suggested to effect this separation. In a recent issue of the *Zeitschrift für angewandte Chemie* (1895, p. 530), Olav Steen reviews thirteen of these methods and concludes that an early proposal of Rose,[1] in which the lead is thrown out as chloride and weighed as sulphate, another by Löwe,[2] in which the bismuth is removed as basic nitrate, and a late suggestion made by Jannasch,[3] *viz.*, the expulsion of the bismuth as bromide from a mixture of lead and bismuth sulphides by an air current carrying bromine are the most satisfactory. At least these methods gave Steen the best results. The separation of bismuth from lead frequently confronts the analyst, and any novelty in this direction cannot be absolutely devoid of interest, hence the present communication, which brings data that may perhaps prove of service in the hands of others who are interested in the solution of this analytical problem.

It will be recalled that Herzog[4] proposed to separate bismuth from lead by precipitating the former as basic acetate. The method required considerable time for execution, and in other hands than those of its author apparently has not yielded entirely satisfactory results.

An idea closely related to that of Herzog would be the substitution of a formate solution for that of the acetate. This was done with results that are very interesting.

Solutions of lead nitrate and bismuth nitrate in nitric acid were made up of such strength that twenty cc. of the first contained 0.2076 gram of lead oxide, and twenty cc. of the second 0.1800 gram of bismuth trioxide. The lead and bismuth were accurately determined after dilution to a liter. Twenty cc. of these two nitrate solutions were then introduced into a beaker

1 *Ann. chem. phys. Pogg.*, 110, 425.
2 *J. prakt. Chem.*, 74, 348.
3 *Ber. d. chem. Ges.*, 25, 124.
4 *Ztschr. anal. Chem.*, 27, 650.

glass, carefully diluted and almost neutralized with sodium carbonate, or until the incipient precipitate dissolved slowly, when considerable sodium formate solution of sp. gr. 1.084 and a few drops of aqueous formic acid were added. The total dilution of the liquid was 250 cc. It was gradually heated to boiling and held at that point for *five* minutes. The precipitate was then allowed to subside, but was filtered while yet hot. The basic formate separates rapidly and is easily washed if not boiled too long. It was washed with hot water, then dissolved in dilute nitric acid and precipitated with ammonium carbonate. The ignited bismuth trioxide weighed too much; it contained lead. However, the impure oxide was dissolved in nitric acid, diluted to 250 cc., and after the addition of sodium carbonate to almost complete neutralization, sodium formate and free formic acid were added as before, and *the precipitation of basic formate repeated*. This precipitate after solution and the bismuth thrown out by ammonium carbonate gave 0.1804 gram of bismuth oxide instead of 0.1800 gram as required by theory. Seven additional separations, in which the quantities of bismuth and lead were the same as indicated above, gave:

0.1806 gram of Bi_2O_3.
0.1806 " " "
0.1803 " " "
0.1804 " " "
0.1804 " " "
0.1805 " " "
0.1796 " " "

The conditions in these determinations were similar to those previously outlined.

With a solution containing 0.3600 gram of bismuth oxide and 0.2076 gram of lead oxide, operating in an analogous manner, two results were obtained:

0.3595 gram of Bi_2O_3.
0.3605 " " "

instead of the required 0.3600 gram.

The residual bismuth trioxide was examined for lead, but none was found.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

XLVIII.—ON SOME NEW FORMS OF GAS GENERATORS.[1]

BY THOMAS H. NORTON.

Received August 27, 1896.

IMPROVEMENTS in the construction of the automatic generators, for the gases most frequently used in our laboratories, are always welcome. The following three types, which I devised some time since, have been subjected to prolonged trial in the laboratory of the University, and have given such satisfactory results, that a detailed description would seem worthy of publication.

In Fig. 1 is represented a gas generator for hydrogen, hydrogen sulphide, etc., which differs in several details from well known types of the same general outline. It is constructed of glazed earthenware, and is easily made in our ordinary potteries. *A*, the outside container, is provided with handles on the outside, and is ordinarily sixty cm. in height. Its chief peculiarity is the presence on opposite sides of the inner wall, of the shoulders *DD*, each about four cm. wide and slightly concave on the lower surface. *B*, the gas reservoir, is of the ordinary bell-jar construction, with orifice at the top for the introduction of a perforated stopper and outlet tube. It is provided with projecting shoulders three cm. wide, corresponding to *DD*, and at such a height that they barely slip beneath the latter. At the bottom are frequent circular perforations, one centimeter in diameter, to allow of the easy passage of the acid charge. The recipient *C*, designed to hold zinc or any solid charge, is provided with a loose disk perforated with many fine openings and resting upon the shoulder of the constriction. Beneath the constriction are perforations corresponding to those in *B*. A strong copper wire or rod, passing through the perforations of both parts of the apparatus, holds *B* and *C* in their mutual position to each other.

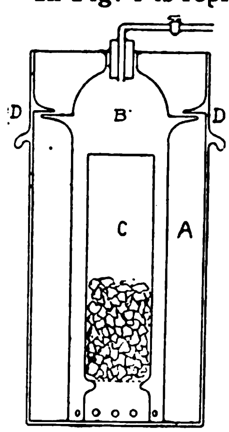


FIG. 1.

[1] Read before the American Association for the Advancement of Science at the Buffalo Meeting.

The working of the generator is exceedingly simple. *C* receives its charge of zinc, marble or ferrous sulphide. *B* is placed over it. The copper rod is passed through the perforations at the bottom. *B* with *C* is then introduced into *A*, and turned until the shoulders of *B* are beneath *DD*. *A* is then filled with the acid charge. The buoyancy of *B* is partly overcome by the rigid attachment of *C*, and entirely prevented by *DD*. Gas can be drawn off as desired, by opening the tap at the outlet tube. When, as naturally occurs, the acid in the lower portion of the generator becomes weak and the evolution of gas sluggish, the exit tap is closed, *B* is turned slightly so as to be free from *DD*, and is then lifted, by grasping the neck, along with the holder *C*, until entirely above the surface of the acid. Both are then plunged to the bottom of *A*, and a few repetitions of this churning movement renders the acid charge of uniform strength.

This style of generator has rendered excellent service. For example, one sixty centimeters in height easily supplies all the hydrogen sulphide required by a class of thirty in qualitative analysis. The special advantages of this generator are to be found in the ease and simplicity with which the buoyancy of the gas reservoir is overcome and the acid charge is maintained at a uniform strength until practically exhausted.

In Fig. 2 we have a less compact and less transportable form, but one which maintains the uniform strength of the acid charge until it is exhausted, without the need of special manipulation, as described above. It is particularly designed for use where small amounts of hydrogen sulphide are in constant requisition, as in the laboratory for qualitative analysis, and it has the advantage of being capable of easy construction from the glassware found in any well equipped laboratory. *A* is a capacious tubulated bell-jar inverted and resting upon

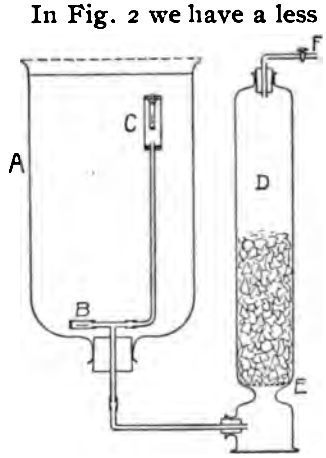


FIG. 2.

either a tripod or the ring of an ordinary support. The perforated stopper in the neck is traversed by a T tube. One terminal of this tube is connected with a simple Bunsen valve, *B*, *i. e.*, a piece of rubber tubing, closed at one end and provided with a clean cut slit in the rubber some two cm. in length. The other terminal of the T tube is connected with *C* in the upper portion of *A*. The attachment *C* is similar to that frequently introduced between suction pumps and filtering flasks. It is the reverse of *B* in its construction, allowing a current of liquid to enter from the outside through the rubber valve. *A* serves as a reservoir for the acid charge. The third external terminal of the T tube is connected with the tubulus of the lower portion of an ordinary lime drying tower, *D*, preferably of the largest size constructed. *D* serves as the recipient for the ferrous sulphide, etc., which may be used, and is provided with a perforated disk at *E* and the outlet tube *F*, the latter on a level with the top of *A*. The working of the generator is exceedingly simple. *A* is charged with acid and *D* with, say, ferrous sulphide. When *F* is opened the acid flows through *C* into *D*. When *F* is closed the pressure of the gas evolved forces the acid back into *A* through *B*. The result is that the supply of acid furnished *D* is always from the top of the reservoir *A*, and hence stronger than that found in the lower strata, which are successively of greater specific gravity, weaker in acid and richer in saline matter, as the bottom is approached. The arrangement permits of a very complete utilization of the acid. When the current of gas is in continuous demand, and evolution becomes sluggish, it is necessary to close the tap at *F* for a short time until the liquid in *D* is driven back into *A*.

Care must be exercised in constructing the valve at *C*, so that it will yield to a very slight pressure. To effect this the slit in the rubber should be at least two cm. in length. When the apparatus is used exclusively for the evolution of hydrogen sulphide to be employed in qualitative analysis, it is desirable to have beyond *F* some device which regulates uniformly the strength of the current of gas and keeps it within the limits of easy absorption. In practice this has been accomplished most simply by introducing into the rubber tube attached to *F* a short

piece of glass tubing, one end of which is drawn out so as to form a very narrow opening.

Essentially the same principle for the control of the strength of the acid charge is to be found in the generator devised recently by Professor Harris. In consequence of the costly character of the latter, due largely to the use of valves of elaborate construction, the form of generator just described may be welcome to many on account of its simplicity and inexpensiveness.

An automatic chlorine generator based upon the use of manganese dioxide, has long been desired. In Fig. 3 is shown such a generator which for six years has rendered satisfactory service, both on the lecture table and in the laboratory. The essential parts only are outlined without the accompanying supports. *A* is a copper funnel, provided with a hollow projection *C*, on one side, perfectly similar in make to the funnels used for hot water filtration. It can be advantageously replaced by the more graceful and modern type of aluminum funnel, resting in a ring burner. The reservoir *B* is of glass, and is an article of current manufacture, obtainable from all dealers in chemical glassware. The long, tapering neck is tightly fastened in the neck of the funnel by means of a section of rubber tubing. A large opening at the top, closed by a rubber stopper, serves for the admission of the charge. In a smaller tubulure on the side is a perforated rubber stopper with outlet tube and tap. The funnel with its reservoir is held firmly in a support, so that the end of *C* is about two cm. above the top of an ordinary burner. A perforated plate is introduced into *B* so as to prevent solid matter from falling into the narrow neck. The latter is connected at *D* with a large tubulated bottle *E*, which serves as a reservoir for hydrochloric acid, and is attached to a support so that it can be raised

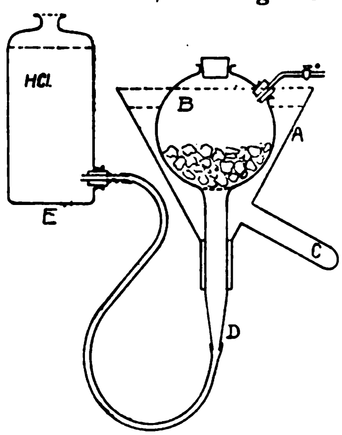


Fig. 3.

or lowered at will. When in use B is filled to two-thirds of its capacity with manganese dioxide, large lumps alone being used, as powdered mineral may easily cause a stoppage of the connections. E is filled with hydrochloric acid and raised to a level slightly above the top of B. Water is poured into the funnel A until it is nearly full, and a lamp is placed under C. As soon as the temperature has reached about 80°, a very small flame suffices to maintain the activity of the generator. When the exit from B is open, the acid enters and the evolution of chlorine continues until checked by closing the tap, when the acid is driven back into E. A slight agitation of the latter before opening the tap serves to prevent the accumulation of a stratum of weak acid at the bottom. It is advisable to lower the reservoir E when a current is not required, so as to avoid pressure and any possible escape through minute leaks. In practice it is also found desirable to connect the opening of E by a flexible tube with a bottle of caustic soda solution, the tube terminating at the surface of the solution. This prevents any escape into the surrounding air of chlorine, with which the contents of E are soon saturated. When thus arranged a current of the gas can be taken at will from the generator, the sole condition being the maintenance of a small flame beneath C. The manifold advantages of such a device, especially for the lecture table, will be appreciated by all who attempt an extended series of experiments with chlorine. As described above the generator can be readily constructed from pieces of apparatus ordinarily found in a well equipped laboratory. I have found a generator in which the reservoir B contains 1500 cc., a very convenient size for use in the lecture room.

MINERAL CONSTITUENTS OF THE WATERMELON.

BY GEORGE F. PAYNE.

Received September 28, 1896.

THE watermelon is not a crop that is widely grown even in this country with great success. It is this very reason which makes it a desirable crop to handle in Georgia, as the watermelons in this state attain finer flavor, crispness, juiciness and sweetness than anywhere else in the world.

Upon analysis of two medium-sized watermelons cut up and mixed together, we found them to contain just one-third per cent. of pure ash, calculated as free from carbonic acid. The exact figures were 0.3338, which in our calculations we will round off into an even one-third, which it practically is.

The composition of watermelon ash is as follows:

	Per cent.
Sulphur trioxide	4.41
Calcium oxide	5.54
Magnesium oxide	6.74
Potassium oxide	61.18
Sodium oxide	4.31
Silicon dioxide	2.15
Phosphorus pentoxide	10.25
Chlorine	4.94
Iron sesquioxide	0.48
Total	100.00

A good average crop of watermelons is considered to be about one-half carload to the acre, though much larger crops than this are sometimes made. Large watermelons are also considered desirable, hence in considering what is carried off from the land by the removal of the crop, it is well to consider how much would be taken off by a large crop, as it is the large crops which we desire to produce. We have before us a report of a crop of watermelons upon an acre of land which is an unusually large one, but which was weighed up in the presence of disinterested witnesses and sworn to by them as being honestly grown upon an acre and correctly weighed. This crop weighed 39,766 pounds. One-third per cent. of such a crop would be pure ash, and consequently the mineral plant food taken out of an acre of land by such a crop would be as follows:

	Pounds.
Sulphur trioxide	5.85
Calcium oxide	7.34
Magnesium oxide	8.93
Potassium oxide	81.09
Sodium oxide	5.71
Silicon dioxide	2.85
Phosphorus pentoxide	13.59
Chlorine	6.55
Iron sesquioxide	0.64
Total	132.55

In the crop mentioned above to replace the phosphoric acid and potash carried off from one acre by the melons alone, not taking into account the vines and roots, would require:

	Pounds.
Acid phosphate (thirteen per cent. P_2O_5)	100
Muriate of potash (fifty per cent. K_2O)	160

A fair crop of melons upon good land, however, is usually considered to be about one-third of the above large crop or about one-half carload. If we estimate then the amounts of phosphoric acid and potash required for an average crop of fair character, such a crop will take from the soil materials to replace which will require about:

	Pounds.
Acid phosphate	33⅓
Muriate of potash	53⅓

This will give about four and one-half pounds of available phosphoric acid to an acre, and about twenty-seven pounds of pure potash to an acre. The usual goods on the market guarantee about ten per cent. of available phosphoric acid and about one per cent. of potash. The use of 300 pounds of such goods upon each acre of watermelons, furnishes thirty pounds of available phosphoric acid, or about six and one-half times as much as is needed to replace what is carried off by the watermelons. It also furnishes about three pounds of potash, which is only one-ninth of what is carried off by the crop removed. This being the case it shows with what advantage and economy the watermelon grower can replace a large proportion of his phosphoric acid with potash.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 22.]

A MODIFIED FORM OF THE EBULLIOSCOPE.

BY H. W. WILEY.

Received September 26, 1896.

THE determination of the alcohol in wines and beers, from the temperature of the vapors given off on boiling at atmospheric pressures, has long been practiced. The instrument by means of which this determination is made is known as the ebullioscope or ebulliometer. The use of this instrument

was proposed many years ago by Tabarié, and it has been improved by Malligand, Salleron and others.

It is evident that if so simple an apparatus could be made to give accurate data, it would come into general use for ordinary purposes. The difficulties which have attended the use of the ebullioscope, however, have been of such a nature as to render the data given by it somewhat unreliable. Among these difficulties may be mentioned the fact that a wine or beer contains a considerable quantity of dissolved matters, which serve to render the temperature of the boiling liquid higher than the temperature of a mixture of a similar percentage of alcohol with water. While the temperature of the vapors emitted are, theoretically, not influenced in a marked degree by the initial temperature at which they are formed, nevertheless, in practice it has been shown that the tendency of the higher initial boiling point is to give a higher reading to the thermometer whose bulb is surrounded by the emitted vapors.

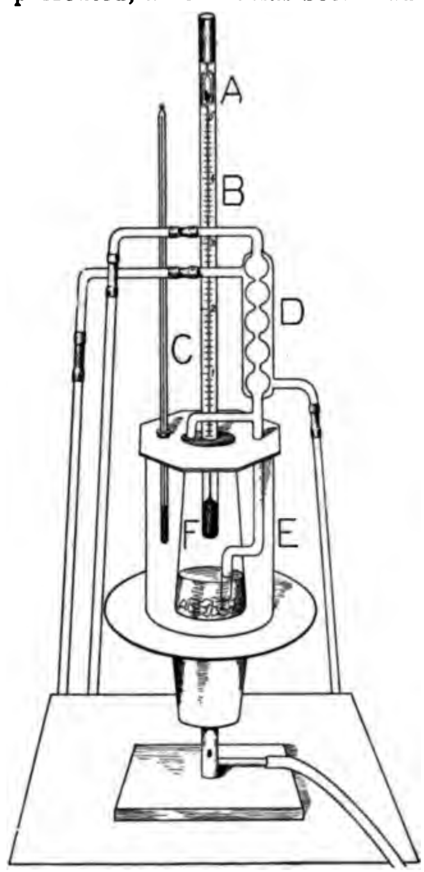
Another difficulty attending the use of the ebullioscope is found in the fact that the percentage of alcohol in the vapors emitted is much greater than in the residual liquid. As a result, it is difficult to establish a balance between the condensed vapors and the liquid remaining in the flask, in such a manner as to secure a continuous evolution of a vapor containing a definite proportion of alcohol.

In the third place, it has been customary to return the condensed vapors through the apparatus in such a way that they come in contact with the uncondensed vapors surrounding the thermometer. By this means the vapors surrounding the bulb of the thermometer are subjected to changes of temperature which render it difficult to get a mean reading of the height of the mercurial column in the instrument. The variations which the mercurial column may undergo amount, in some instances, to two or three-tenths of a degree and as each tenth of a degree represents approximately a tenth of a per cent. of alcohol, it is not difficult to see that these variations would tend to lead to erroneous results.

In the fourth place, barometric changes, which are constantly taking place in the atmosphere, change the boiling point of the

vapor of water so that it is frequently necessary to check the instrument with pure water, in order to have an initial temperature for the calculations.

In the apparatus which is presented, an effort has been made to remedy the difficulties which have been mentioned above. The apparatus consists of the flask *F*, which is closed by a rubber stopper carrying the large thermometer *B* and a tube leading to the condenser *D*. The vapors which are given off during ebullition are condensed in *D* and return to the flask through the tube, as indicated in the figure, entering the flask below the surface of the liquid therein.



The flask is heated by a gas lamp and is placed upon a circular disk of asbestos in such a way as to entirely cover the hole in the center of the asbestos disk, which is a little smaller than the bottom of the flask. The whole apparatus is protected from external influences of temperature by the glass cylinder *E*, which rests upon the asbestos disk below and is covered with a detachable, stiff rubber cloth disk above.

The thermometer *C* indicates the temperature of the ambient air between *F* and *E*. The reading of the thermometer *B* should always be made at a given temperature of the ambient air, as indicated by *C*. The tube leading from the top of the conden-

ser D to the left, is made long and is left open at its lower extremity, in order to secure atmospheric pressure in F, and at the same time prevent the diffusion of the alcohol vapors through D.

The flame of the lamp is so regulated as to bring the temperature of the thermometer C to about 90° in ten minutes for substances not containing over five per cent. of alcohol. After boiling for a few minutes, the temperature, as indicated in the thermometer B, is constant, and the readings of the thermometer should be made at intervals of about half a minute for two minutes. Some pieces of scrap platinum placed in the flask will prevent bumping and secure a more uniform evolution of vapor.

Slight variations, due to the changes in temperature of the vapor, are thus reduced to a minimum effect upon the final results.

The apparatus is easily operated, is quickly charged and discharged and with it at least three determinations of alcohol can be made in an hour.

The thermometer used is the same as is employed for the determination of freezing and boiling points in the ascertainment of molecular weights. The reading of the thermometer is arbitrary, but the degrees indicated are centigrade. The thermometer is set in the first place by putting the bulb in water containing sixteen grams of common salt to 100 cc. When the water is fully boiling, the excess of mercury is removed from the column in the receptacle at the top and then, on placing in ordinary boiling water, the column of mercury will be found a little above the 5° mark. This will allow a variation in all of 5° in the temperature, and a thermometer thus set can be used for the estimation of percentages of alcohol from one to five and a half, by volume. When the liquor contains a larger percentage of alcohol than this, it is advisable to dilute it until it reaches the standard mentioned.

In order to avoid frequent checking of the thermometer, rendered necessary by changes in barometric pressure, I use a second apparatus made exactly as the one described, in which

water is kept constantly boiling. It is only necessary in this case to read the two thermometers at the same instant in order to make any necessary correction required by changes in barometric pressure.

It is not my purpose here to submit a table showing the percentages of alcohol corresponding to any given depression in the temperature of the boiling vapor. It is only necessary to call attention to the fact that for the percentages named, the platted line showing the variation in depression from 0° to five per cent. by volume of alcohol is practically straight and that for each 0.8° change in the boiling point of the vapor, there is a change of about one per cent by volume of alcohol. This rule can be safely applied for practical purposes to all liquors containing not more than five and five-tenths per cent. of alcohol. For instance, if, in a given case, the temperature of the vapor of boiling water, as marked by the thermometer, is 5.155°, and the temperature of the vapor of a sample of beer is 2.345°, the depression is equivalent to 2.810°, and the percentage of alcohol by volume is therefore 2.81 divided by $0.80 = 3.51$.

The thermometer used is graduated to hundredths of a degree and is read by means of a cathetometer, which will easily give readings to five thousandths of a degree.

The reading of the thermometer is facilitated by covering the bulb with a test-tube containing water. The high specific heat of the water distributes evenly any little variations of temperature which otherwise would cause the mercurial column in thermometer *B* to oscillate. The water jacket also serves as a protection against the projection of any particles of the boiling liquor directly against the bulb of the thermometer.

It is believed that this apparatus is the best form of ebullioscope which has yet been offered for practical use to analysts.

VOLUMETRIC DETERMINATION OF ACETONE.[1]

By Edward R. Squibb.

Received November 9, 1896.

IN the *Moniteur Scientifique* of 1893, 41, 4 Serie, Vol. 7, 1°, p. 272–274, MM. J. Robineau and G. Rollin publish a paper entitled, "Dosage Volumetrique de L'Acetone," and the following is, first, a free translation and abridgement of this paper; and second, the detail of an improvement of the process whereby it is rendered easier, more simple, quicker, and better adapted to technical uses, whilst still sufficiently accurate for most purposes.

FIRST, FREE TRANSLATION.

The common way of determining the proportion of acetone in a liquid containing it is to convert the acetone into iodoform by means of iodine in the presence of soda after eliminating from the liquid everything that would interfere with the proper reaction.

For this process binormal solutions of iodine and of sodium hydroxide are used, and the precipitated iodoform is washed, dried, and weighed, or is dissolved in ether, and the whole or a fraction of the ethereal solution is dried over sulphuric acid and weighed.

The appreciable volatility of iodoform at ordinary temperatures introduces a source of error that is objectionable, especially when dealing with small quantities.

But, aside from this, the time required for this process is relatively so long that we have sought to change it to a volumetric process that is more rapid.

Our proceeding consists in mixing the acetone with a solution of potassium iodide and sodium hydroxide, and then transforming it into iodoform with a titrated solution of a hypochlorite. The end reaction is indicated by the appearance of a blue color, when a drop of the liquid is touched with a drop of bicarbonated starch solution.

From the quantity of hypochlorite used the quantity of acetone is deduced.

[1] Read before the New York Section of the American Chemical Society, November 6th, 1896.

For it happens that the presence of even the smallest trace of an alkaline hypoiodite, in a solution of soda, gives a blue color with a starch solution which contains an excess of sodium bicarbonate.

Again, a liquid containing acetone, an iodide and caustic soda in excess, and into which a solution of hypochlorite is passed, gives no reaction with bicarbonated starch until the whole of the acetone is converted into iodoform.

This proceeding, however, only gives constant results when certain precautions are taken. Unless the liquid containing the acetone be sufficiently alkaline, an excess of hypochlorite will be required to decompose all the acetone.

The potassium iodide must be in excess.

The dilution must be fairly uniform, and the concentration of the hypochlorite about the same for the different titrations.

The process should not be used in too strong a light.

It is very important that the liquid should be constantly stirred during the additions of the hypochlorite.

The strength of the hypochlorite solution is ascertained by trial against a pure acetone made by the bisulphite process.

PREPARATION OF THE HYPOCHLORITE.

For the titration of liquids containing considerable proportions of acetone, the hypochlorite solution is prepared as follows:

To 500 cc. of the concentrated solution of sodium hypochlorite of commerce, which tests from forty-five to fifty-five volumes of chlorine, an equal measure of water, and ten cc. of solution of pure soda of 36° B., are added, and the solution is kept in an amber colored bottle, well corked.

TITRATION OF THE HYPOCHLORITE SOLUTION.

About two grams of pure acetone from bisulphite is weighed off and diluted to 500 cc.

Then ten grams of pure potassium iodide is put into a conical Bohemian beaker and 100 cc. of the diluted acetone and twenty cc. of solution of caustic soda of 28° B. are successively added, and the whole is stirred until the iodide is dissolved and the liquid is homogeneous.

Into this the hypochlorite solution is passed drop by drop from a burette, with constant stirring, precipitating the iodoform in large flakes which easily settle out. When farther additions of the hypochlorite give but a light cloudiness a drop of the liquid is transferred to a white porcelain plate by means of a glass rod and is there brought in contact with a drop of the bicarbonated starch solution. As soon as the hypochlorite is in excess the blue color appears very distinctly. The volume of hypochlorite used is then read off from the burette, and then for security of result the titration is repeated.

Example.—2.081 grams pure acetone is weighed off and diluted to 500 cc; 100 cc. of this solution requires 22.5 cc. of the hypochlorite. This gives for each cc. of hypochlorite 0.01874 gram of pure acetone. These results are liable to vary a little if the conditions of the experiment vary much. The stirring is supposed to be constant, and the hypochlorite solution to be regularly added.

If to 100 cc. of the diluted acetone 100 cc. of water be added and the same quantities of iodide and soda as above, 22.05 cc. of hypochlorite is required instead of 22.5 cc. In using forty cc. of the soda solution instead of twenty cc., twenty-two cc. of the hypochlorite is required. In using sixty cc. of soda solution instead of twenty cc., 21.6 cc. of the hypochlorite is required. In using ten cc. of soda instead of twenty cc., twenty-three cc. of the hypochlorite is required.

These results show that dilution of the acetone and a small excess of soda have but little influence, but that a deficiency in alkalinity has a very considerable effect on the quantity of hypochlorite required. And farther, that the alkalinity indicated by twenty cc. of soda solution of 28° B. appears to be normal.

Under the given conditions of alkalinity and dilution tne relations between acetone and the available chlorine of the hypochlorite is obviously one molecule of acetone to six atoms of chlorine.

The solution of hypochlorite used by us was the liquor of Penot, testing 21.56 volumes.

The titration of the hypochlorite with pure acetone may be

omitted, simply determining the available chlorine of the liquor of Penot instead, but we prefer the titration with pure acetone.

DETERMINATION OF ACETONE IN A COMPLEX LIQUID.

We give as an example of this the titration of a complex liquid made with precision, which liquid has served us to control the accuracy of the process.

The complex liquid contained:

1.510	grams	water,	39.98 per cent. acetone.
1.677	"	ethyl alcohol,	
1.550	"	methyl alcohol, pure	
3.149	"	acetone, pure from bisulphite	

Of this mixture 3.2445 grams was weighed off and diluted to 500 cc. Proceeding as before 100 cc. of this dilution, ten grams of potassium iodide, and twenty cc. of soda solution of 28° B. required 13.85 cc. of the hypochlorite. This by calculation gives 39.99 per cent. of acetone, and thus verifies the composition of the complex liquid; and it is seen that the presence of ethyl alcohol is without influence on the result.

The effect of the presence of paraldehyde in the same complex liquid was tried by a similar titration.

To 100 cc. of the complex solution corresponding to 0.4162 gram of pure acetone, ten cc. of an aqueous solution containing five per cent. of pure paraldehyde was added (say one-half gram) or a little more paraldehyde than acetone. This mixture took 22.4 cc. of the hypochlorite instead of 22.2 cc. as required.

This variation is slight for the relatively large proportion of paraldehyde, and is greater for larger proportions, but instances are rare in which paraldehyde is present in such proportions.

In all such instances where the presence of the aldehyde has been established by the process of Bardy, the acetone should be purified by this process before titration.

For the determination of acetone in very dilute solutions a solution of hypochlorite of one-fifth of the above strength is preferred. That is, a solution containing four or five volumes of available chlorine, and the degree of alkalinity should be proportionately reduced.

With a little practice it is easy to judge as to how much acetone is present in a liquid to be titrated, and from this to judge

of the corresponding quantity of hypochlorite required, and in this way keep the conditions of the method nearly uniform, and the more uniform the conditions the more constant the results.

This process has the great advantage of being rapid, and thus of permitting a number of titrations being made in a short time with results sufficiently accurate.

REMARKS.

The reaction used in this titration is very delicate, and where traces of acetone are concerned it is better seen when there is excess of iodide and of soda and but little hypochlorite. An aqueous solution of 0.004 gram of acetone in the liter gives a heavy cloudiness immediately. The reaction with 0.0012 gram of acetone in the liter is seen in a few moments. With 0.0008 gram to the liter the reaction is difficult to see. This reaction should not be made in a bright light. In sunshine or in a very bright light the traces of iodoform produced disappear very rapidly, the liquid becoming clear, but in a dim light the precipitate does not disappear.

The titrated solution of hypochlorite should be kept in amber-colored glass in a cool place and sheltered from bright light. The titration should be frequently repeated, because it varies rather rapidly, especially when diluted. We have made a series of experiments on this point, which strikingly show these variations under different influences. A solution of hypochlorite prepared for titrations gave 22.16 volumes of available chlorine; kept in a cool place, in obscurity for six days, it gave 21.96; kept in colorless glass, corked, in a bright light, most of the time in sunlight, for seven days, it gave 12.32. In a water-bath at 100° C. for a quarter of an hour it gave, when cooled, 19.48.

END OF TRANSLATION.

The rapidly increasing uses of acetone in the three years that have passed since the publication of this important paper of Robineau and Rollin have given to it so much additional importance that it seemed well to the present writer—who early adopted this volumetric method—to attempt to modify the method in the direction of greater simplicity and rapidity, even

if this should be at the cost of a little of its accuracy. As acetone comes more and more to take the place of both ethyl and methyl alcohol as much the better solvent for most purposes, and as its manufacture is cheapened, it becomes more and more desirable to have a rapid and easy way of estimating its proportions in mixtures or under conditions to which specific gravity is not applicable.

Therefore, taking the above quoted paper as a basis, and giving full credit to the authors of it for every important principle and step of the method, the following slight modifications are offered as the result of about three months' experience with the original process and over a year's experience with the modifications.

STANDARD SOLUTION OF ACETONE.

A flask of 100 cc. capacity containing about fifty cc. of distilled water is carefully weighed. To this is added about thirteen cc. of pure acetone, made by the bisulphite process. The weight is then again taken, when it will be found that the acetone added is a fraction more or less than ten grams. The dilution is then transferred to a measuring flask, the weighing flask being rinsed in and is farther diluted with distilled water until each ten cc. of the dilution contains one-tenth gram of acetone. This is kept in a well stoppered bottle of dark glass, for, although the writer has no evidence of any change taking place in acetone, and believes it to be quite as permanent as ethyl alcohol, still it may be well to keep a dilute standard solution protected against bright light.

Of this solution or dilution ten cc. equal to one-tenth gram of acetone, is accurately measured off for each titration of the solution of hypochlorite.

SOLUTION OF POTASSIUM IODIDE.

Of this salt 250 grams are dissolved in distilled water, and the solution is made up to one liter, when each ten cc. will contain two and a half grams of the iodide.

SOLUTION OF SODIUM HYDROXIDE.

Of commercial caustic soda, purified by alcohol, 257 grams is dissolved in distilled water, the solution made up to one liter,

and set aside until it settles quite clear. Then 850 cc. of clear solution is poured off and added to the solution of potassium iodide, making 1,850 cc. of total solution.

Of this solution twenty cc. is taken for each titration.

The remainder of the soda solution is again allowed to settle clear for farther use in the hypochlorite solution.

SOLUTION OF SODIUM HYPOCHLORITE.

The officinal solution of chlorinated soda of the U. S. Pharmacopœia ("Liquor Sodæ Chloratæ," U. S. P.) answers very well for this process, the officinal strength of two and six-tenths per cent. of available chlorine being quite convenient.

To a liter of this solution in a bottle of dark glass, twenty-five cc. of the above described clear soda solution is added and the mixture well shaken.

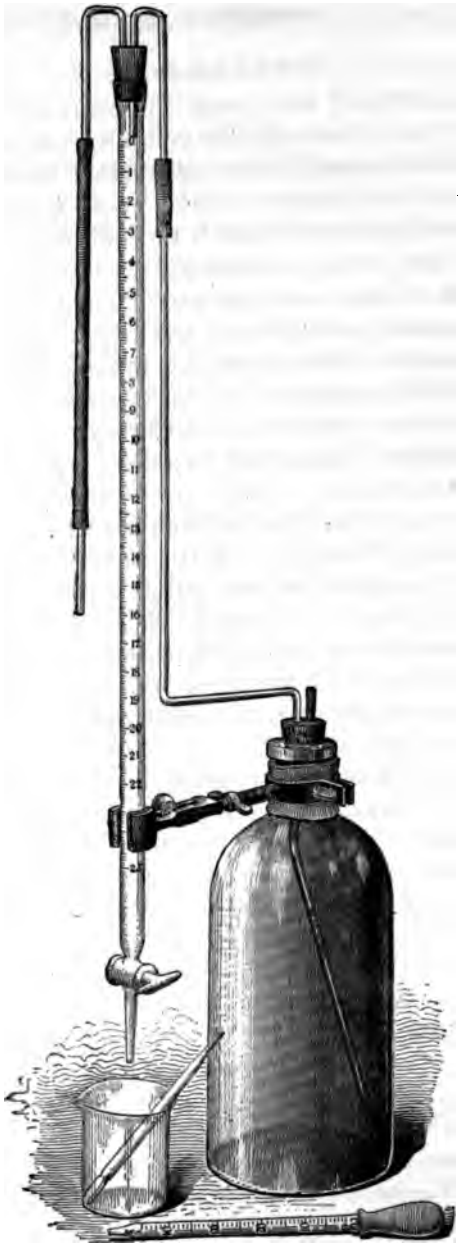
If in buying the "Solution of Chlorinated Soda" of the U. S. P. for this process it should be found, as is not unfrequently the case, weaker than is required by the U. S. P., or, if by keeping it becomes weaker, this will be at once discovered on balancing it against the standard acetone solution, and so long as the one-tenth gram of acetone does not require more than say twenty cc. of the more dilute hypochlorite, the formula need not be modified.

If there be much of this titration to do it is very convenient to fit this bottle with an automatic zero burette,[1] as shown in the following illustration, this form being, so far as is known, original with the writer and very convenient for general rapid working with a burette. The advantage is, beside that of rapid and easy working, that it does not require a special burette and is easily fitted up from the resources of any laboratory.

BICARBONATED STARCH SOLUTION.

Starch, 0.125 gram, is mixed with five cc. of cold water, and then added to twenty cc. of boiling water and boiled. When cold two grams of sodium acid carbonate is added and stirred until dissolved. Kept in a colorless bottle this solution does not sensibly diminish in delicacy or reaction in three months. But for how much longer it would remain good for this reaction was not tried.

[1] This Journal, 16, 145.



Automatic Zero Burette.

THE TITRATION.

The burette being filled with the solution of sodium hypochlorite, ten cc. of the standard solution of acetone (equal to one-tenth gram of acetone) is measured into a beaker of about fifty cc. capacity, and twenty cc. of the mixed solution of iodide and soda is added and stirred well. Into this the hypochlorite solution is passed in rapid dropping, with constant stirring, until eight or ten cc. has been run in. Then the precipitated iodoform is allowed to settle out, and a drop or two more hypochlorite is added. Should this produce a dense cloudiness one-half cc. more hypochlorite is added, and well stirred and again allowed to settle. Then a drop or two more of hypochlorite is added. If there should still be a cloudiness, another one-half cc. of the hypochlorite is added and well stirred, and so on until the cloudiness is very slight. Then the starch testing begins.

A small drop of the liquid is transferred by a rod to a white porcelain tile or plate, and a similar small drop of the starch solution is placed very near it. Then with the first rod the drops are made to connect by a fine line, so that the whole has a dumb-bell form. If there be no blue color, one or two-tenths cc. more of the hypochlorite is added and well stirred, and the testing is repeated, until finally a blue line will be seen at the moment of contact of one drop with the other. If the last negative testing has taken 10.4 cc. from the burette, and this positive testing, which has given the blue line, required 10.6 cc., then the accepted reading would be 10.5 cc., and this would be the hypochlorite equivalent of one-tenth gram of acetone. If the blue line be very faint, it will be momentary only, and will indicate that the excess of hypochlorite is very small, and that 10.6 cc. is a closer reading than 10.5, but the process is not sufficiently accurate to take much account of such differences, since even with much experience and great care it is hardly practicable to get any two titrations to agree within one-tenth cc. of hypochlorite.

Having then 10.5 cc. as the hypochlorite equivalent of one-tenth gram of acetone at this time, it is easy to estimate any smaller or larger quantity of acetone that requires a smaller or

larger quantity of the hypochlorite by the equation 10.5 : 0.1 : : $a : x$.

But this hypochlorite solution is liable to diminish in strength by keeping, and therefore must be standardized by this standard acetone solution as often as the accuracy of the determinations may require. At times the change in strength is scarcely perceptible from day to day in several successive day's work, but in standing for a week or two there will always be a falling off in strength to the extent of one-tenth to five-tenths cc. in the hypochlorite. The addition of the soda solution appears to render the hypochlorite more permanent, just as the sodium bicarbonate renders the starch solution more permanent. But in the case of the starch the blue reaction does not occur if the bicarbonate be not present.

The titration of the acetone present in unknown dilutions requires first that the strength should be estimated by known conditions or by sensible properties, in order to keep the proportions of the reagents and the dilutions approximately the same, or at least not differing very widely when close determinations are required. If then the taste and smell should indicate that the acetone to be tested is below twenty-five per cent., four-tenths cc. may be taken for the testing. If over twenty-five per cent. and under fifty per cent., two-tenths cc. may be taken. If over fifty per cent., one-tenth cc. is sufficient.

For the adjustment of these small quantities with a sufficient degree of accuracy for rapid technical working, it is convenient to have a five-tenths cc. pipette divided in 0.01 cc. fitted with a rubber bulb, as shown in the illustration. By screwing the neck of this bulb up or down upon the glass, with the point in the liquid, close measurements may be quickly made.

A beaker of fifty cc. capacity containing ten cc. of water is weighed and the weight noted. The four-tenths, two-tenths, or one-tenth cc. of the sample to be titrated is delivered in the water and the weight again taken to give the quantity of the sample taken for the titration. Then the twenty cc. of the iodide and soda solution is added, the whole well stirred, and the hypochlorite dropped in, and the end reaction managed precisely as described in standardizing the hypochlorite, and the quantity of

hypochlorite used is noted. Then as 10.5 cc. of the hypochlorite is to one-tenth gram of acetone, so is the quantity of hypochlorite now used to the quantity of acetone present in the portion of the sample taken for titration. Then as the weight of this portion taken for titration is to the quantity of acetone found in it, so is 100 to the percentage of acetone in the sample.

For example, a sample supposed to be not far from absolute is to be titrated. A fifty cc. beaker with ten cc. of water weighs 25.283 grams; with one-tenth cc. of the sample added the weight becomes 25.360 grams, giving 0.077 gram as the weight taken for the titration. To this is added the twenty cc. of iodide and soda solution, and the mixture being well stirred, the hypochlorite is dropped into saturation when seven and nine-tenths cc. is found to have been used. Then as 10.5 is to one-tenth, so is seven and nine-tenths to 0.0752 gram of acetone in the 0.077 gram of the sample taken. Then as 0.077 gram of the sample taken is to the 0.0752 of acetone indicated, so is 100 to 97.66 per cent. of acetone in the sample.

This is the rationale of the operation, but the calculation is shortened by simply dividing the standard hypochlorite (10.5 cc.) into the hypochlorite required (seven and nine-tenths cc.) to get the corresponding acetone (0.0752 gram), and then dividing the weight of the sample taken (0.077 gram) into the weight of acetone obtained from it (0.0752 gram) to get the percentage proportion of the acetone (97.66 per cent.).

Of course the method of definite dilution, and the titration of an aliquot part, as described in the original paper of Robineau and Rollin (see translation) is available and more accurate than that here recommended, and takes but little more time.

Where acetone is made, or is much used, and especially in processes where it is recovered by distillation to be used over again, there is often much need of testing the strength of very weak dilutions, and of knowing when acetone is absent. In many such uses accuracy is not required and rough estimates are sufficient. For work of this kind, especially when the strength is below ten per cent., the weighing of the sample to be tested may be omitted, because the specific gravity is so nearly

that of water that the measure may be accepted as cubic centimeter for gram.

DETERMINATION OF ACETONE IN THE PRESENCE OF ETHYL ALCOHOL.

The standard dilution of acetone containing ten grams in the liter was used, and ten cc. of this required 14.3 cc. of the hypochlorite solution. On repetition 14.4 cc. was required.

A dilution of ethyl alcohol was made containing ten grams in the liter, and ten cc. of this requires one-tenth cc. of the hypochlorite. On repetition 0.125 cc. was required.

To ten cc. of the acetone dilution two-tenths cc. of the alcohol dilution was added, and this mixture required 14.4 cc. of the hypochlorite solution. On repetition 14.4 cc. again was required.

To ten cc. of the alcohol dilution two-tenths cc. of the acetone dilution was added, and this mixture required 0.35 cc. of the hypochlorite. On repetition four-tenths cc. was required.

In each case ten cc. of the iodine and soda solution was used and all other conditions were kept fairly uniform.

In the case wherein the hypochlorite was added to alcohol alone no precipitate nor cloudiness was visible, although 0.1 to 0.125 cc. was required to obtain the starch reaction. When acetone had been added to the alcohol one-half this quantity of the hypochlorite was sufficient to give decided cloudiness.

These results appear to confirm the conclusions of Robineau and Rollin to the effect that the presence of ethyl alcohol has no effect upon the titration of acetone by this method, although ethyl alcohol is an iodoform-yielding substance. The small quantity of hypochlorite required to obtain the starch reaction when alcohol alone was titrated was probably in consequence of traces of impurity in the alcohol.

THE DETERMINATION OF SULPHUR IN CAST IRON.

By Francis C. Phillips.

Received November 10, 1896.

IN a paper read before the American Chemical Society in August, 1895,[1] I have detailed some experiments made in the determination of sulphur in white cast iron by the evolution method, and have attempted to show that the loss of sulphur in its

[1] This Journal, 17, 891.

determination in such iron may be due to the formation of organic sulphur compounds not oxidizable to sulphuric acid by the usual means.

By passing the gases evolved during the solution of the iron in hydrochloric acid through a heated porcelain tube it was found that the volatile organic sulphur compounds may be decomposed and nearly all the sulphur recovered by conversion into hydrogen sulphide, oxidation and precipitation as barium sulphate.

In judging of the correctness of an analytical method it has been necessary in the case of the majority of the constituents of iron to depend upon a single criterion; that method is regarded as most accurate which, being correct in its details, yields the highest percentage of the constituent sought to be determined. For it is hardly possible to add to pure iron a known percentage of sulphur, phosphorus or carbon, and test the method by a determination of the added constituent. For the determination of sulphur in iron it has been common to regard the method of oxidation and solution of the iron by nitric acid, followed by precipitation of the sulphur in form of barium sulphate as the most accurate, inasmuch that it yields results somewhat higher than those obtained by other modes of procedure.

It does not seem probable that an appreciable error could occur in the use of this method unless, in the simultaneous oxidation of the carbon and sulphur of the iron, an organic sulphur compound should be formed.

It has seemed to be of interest, however, to apply a method for the determination of sulphur by which all the constituents of the metal could be completely oxidized in a dry state and at a high temperature, in order to avoid as effectually as possible the chances of loss due to the conversion of sulphur into a volatile compound not oxidizable by ordinary means to sulphuric acid.

In searching for a method which should answer these requirements, it seemed possible that by heating the iron in the form of fine powder in presence of a mixture of alkaline carbonate and nitrate the sulphur might be oxidized directly and completely to the condition of a sulphate without affording an opportunity

for the escape of a trace of sulphur in some intermediate volatile or soluble compound. Accordingly an experiment was tried in the following way:

An iron containing its carbon in the combined form was melted in a crucible and poured while fused into water. The granulated metal was crushed in a steel mortar to an extremely fine powder. The powder so obtained was sifted through bolting sheeting.

Two and one-half grams of the sifted iron were mixed with ten grams of a mixture of equal parts of sodium nitrate and carbonate in a platinum crucible. The crucible was covered and heated over a Bunsen burner. At a red heat a sudden and rather violent reaction occurred, and having been begun, was easily maintained with very little aid from the burner flame. The reaction appeared to be complete in a few minutes. After heating for a half hour the crucible was cooled and its contents softened in water. A residue of a reddish brown powder, consisting of ferric oxide with a little ferrous oxide, was obtained. This residue was found to contain no sulphuric acid, and on digesting with hydrochloric acid dissolved without effervescence, showing that none of the particles of the original iron had remained unoxidized. From the results of this experiment and others which need not be detailed here, it seemed to be possible to oxidize finely divided iron so completely by heating with sodium carbonate and nitrate, that its sulphur might be converted quantitatively into sulphuric acid.

The mixture of sodium carbonate and nitrate although tending to oxidize finely divided iron, seems to exert a less powerful action upon the carbon contained in the iron, and this carbon may appear as a black residue after the fused mass has been softened and extracted by water and the ferric oxide dissolved in hydrochloric acid.

It seems to be important for the success of the method that in the oxidation of the iron the carbon should also be nearly or completely oxidized, for if the carbon remained unburned a portion of the sulphur might escape oxidation. In general it may be said that the order of oxidation of these three elements by the method used is as follows: 1, iron; 2, carbon; 3, sulphur; the

iron being the most easily oxidized, and the sulphur the most difficult to oxidize. This order is not exactly what we should anticipate, but it is to be remembered that unless the iron grains are fine enough to be penetrated by oxygen, and changed completely into a soft powder of ferric oxide, the sulphur and carbon have no opportunity to oxidize at all. If the iron could be used as an impalpable powder the order of oxidation would probably be different. The marked resistance of the carbon to oxidation has been frequently observed, even when using more sodium nitrate in the fusion than is theoretically enough to completely oxidize both iron and carbon, supposing that the sodium nitrate is reduced only to nitrite in the process.

Experiments of a similar kind were tried with ferromanganese. A metal containing about eighty per cent. of manganese was used. By crushing in a steel mortar this iron was very easily reduced to a powder fine enough to pass through bolting sheeting. On heating the powder with the mixture of sodium nitrate and carbonate a most violent reaction occurred, the metal burning with a long flame, extending several inches above the crucible. In order to control the reaction it was found necessary to melt one-half of the fusion mixture to be used in the crucible and then add slowly the other half, previously mixed with the powdered metal, while stirring constantly. In this way the reaction could be easily controlled. On softening the fused mass in water it was found that the iron had been peroxidized and the manganese changed to binoxide. No trace of sodium manganate was ever formed, the solution in water being after filtration invariably colorless. No carbon was found in the residue. The oxidation of the carbon is much more easily effected in the case of iron containing a high percentage of manganese. In all the trials made the silicon of the iron was oxidized, but it was found that when the fused mass is softened in water very little silica enters into solution as an alkaline silicate, the greater portion remaining insoluble and in a flocculent form.

Experiments were then tried with a gray iron. This form of iron could not be crushed to a fine powder, and an experiment was made in reducing it from small drillings by means of a

chilled iron rubber and plate, such as is ordinarily used for grinding ores. Several gray irons were tried in this way. Some could not be powdered by the method just mentioned, the grains tending to flatten instead of being crushed. Others were readily reduced, but the powder was not in any case fine enough for sifting through bolting sheeting. It was found in the case of a gray iron reduced to powder by the method of grinding, that on fusion with the mixture of sodium nitrate and carbonate, used in the preceding experiments, the graphitic carbon of this iron was more readily burnt than the combined carbon of white iron.

As it had proved to be a somewhat difficult matter to oxidize completely the carbon of the iron in the various experiments made with the fusion method, notably in the case of white iron, some trials were made in the use of sodium peroxide. This proved to be a more efficient oxidizing agent for iron and its contained carbon than sodium nitrate. For these trials a mixture was used consisting of forty-five parts each of sodium peroxide and sodium nitrate, together with ten parts of sodium carbonate.

White iron was oxidized and its carbon burnt during a fusion lasting less than ten minutes.

On heating ferromanganese with this mixture the iron was found to be completely oxidized. The carbon was burnt and the manganese was oxidized and converted into sodium manganate, yielding a deep green solution when the fused mass was digested in water.

An admixture of sodium carbonate to sodium peroxide tends in all cases to diminish its action upon finely divided iron at a high temperature and renders the process more easily controlled. It seemed to be possible to base a method for the quantitative determination of sulphur in certain kinds of cast iron upon the reactions described above.

An indispensable condition of success in the use of the method is found in the extreme fineness of the iron. In the case of white irons the fineness of the powder has been secured by

crushing in a steel mortar until the powder passed through a sieve of bolting sheeting or bolting cloth.[1]

Some gray irons cannot be crushed or ground. To these the method is not applicable. For gray irons, however, the evolution method answers all requirements.

The following details are given of the method finally employed:

1. *White iron.*—About one and one-half grams of the finely powdered and sifted metal was intimately mixed with eight grams of the sodium peroxide mixture above mentioned, or with four grams each of sodium carbonate and nitrate. The somewhat violent reaction set up on the application of strong heat to the platinum crucible was completed in a few minutes. The crucible was heated for about twenty minutes in all. After cooling the contents were softened in water, the solution decanted and the residue ground, while wet, in a mortar. The solution and residue were then digested in a beaker on the water-bath for one hour after addition of two cc. of strong bromine water. The liquid was then filtered, acidulated with hydrochloric acid, evaporated to dryness to separate the small portion of silica which had entered in solution and filtered. The sulphuric acid was determined in the filtrate in the usual manner. The barium sulphate obtained was always white. If the fusion mixture contains sodium carbonate and nitrate, but no sodium peroxide, the crucible must be heated for a longer time, but a portion of the carbon of the iron may still remain unoxidized.

2. *Ferromanganese.*—In this case it is better to use a mixture of equal parts of sodium nitrate and carbonate, omitting the sodium peroxide.

Ten grams of the mixture were divided into two portions, one of which was fused in a crucible. The other portion mixed with two or two and one-half grams of the finely powdered iron

[1] Two different materials are sold which are suitable for the sifting. One is called bolting cloth, the other bolting sheeting. The bolting cloth used in these experiments contained about eighty-five meshes to the linear inch, while in the bolting sheeting about one hundred and thirty-five were counted. The material having the smaller number of meshes is made of coarser threads, however, and yields, on account of the smaller openings, a finer powder. Bolting cloth is, on this account, better suited to the preparation of a sample of white iron for a determination of sulphur by the method described.

was then slowly added. Although too violent combustion of the iron is to be avoided, it seems to be important, for the success of the method, that a reaction of decided intensity should occur during the fusion.

Sodium nitrate possesses an advantage over sodium peroxide in its greater purity, the former compound being readily obtainable with practically insignificant traces of sulphur.

Natural gas was the fuel used for the Bunsen burner in heating the charges. This gas was found by repeated experiments, not to contain a sufficient quantity of sulphur to affect the purity of the sodium carbonate when heated in a platinum crucible in the same manner as in the case of the determinations described.

The usual occurrence of sulphur compounds in coal gas would preclude its use in the application of the method.

From the experiments, the results of which are stated in the accompanying table, there seems to be some reason to suppose that not quite all the sulphur of the iron is converted into barium sulphate when the metal is oxidized and dissolved by nitric acid. That it has been completely recovered by the process of fusion cannot be positively asserted.[1]

The method I have described is not proposed as a substitute for any existing method. The purpose of the present work was merely to ascertain as far as possible whether by a process of direct oxidation of the iron in a dry state a larger proportion of the sulphur could be recovered in weighable form than by the usual method of oxidation and solution in nitric acid.

My thanks are especially due to Mr. F. B. Smith for great care and attention to detail in conducting the experiments I have detailed.

[1] The method of preparation of a sample for analysis in the case of the more brittle forms of iron, by crushing in a steel mortar and sifting, is suggested in Regnault's Elements of Chemistry, translated from the French by Betton, 1867, 2, 112.

Character of iron used.	Fusion mixture employed.	Percentage of sulphur found by fusion.	Percentage of sulphur found by the method of oxidation by nitric acid.
White iron A crushed in mortar and sifted through bolting sheeting.	Contained equal parts of sodium carbonate and nitrate.	0.112	0.101
		0.112	0.098
		0.111	0.096
		0.107	0.099
		0.114	0.100
		0.114	0.102
		0.106	0.102
		0.108	0.104
		0.107	
		0.103	
Means		0.109	0.100
White iron B crushed and sifted.	Contained 45 parts $NaNO_3$ 45 parts Na_2O_2 10 parts Na_2CO_3	0.155	0.143
		0.150	0.149
		0.130	0.143
		0.139	0.147
		0.166	
		0.156	
		0.156	
		0.161	
		0.151	
Means		0.151	0.145
Ferromanganese crushed and sifted.	Contained equal parts of sodium nitrate and carbonate.	0.022	0.012
		0.027	0.013
		0.018	0.012
		0.018	0.010
		0.018	
		0.019	
		0.016	
Means		0.020	0.012
Gray iron drillings powdered by rubber and plate. Not sifted.	Contained equal parts of sodium nitrate and carbonate.	0.034	0.027
		0.030	0.030
		0.036	0.026
		0.034	0.028
		0.033	0.028
		0.034	0.022
Means		0.033	0.027

CARBON DETERMINATIONS IN PIG IRON.

By Bertrand S. Summers.

Received October 3, 1896.

THOSE chemists who have had occasion to do many carbon determinations in pig iron, to which was allotted but little time, have probably felt the need of improvements in some of our standard methods.

The old oxygen combustion method, although accurate, requires more time than can usually be spared if use is made of a porcelain or glass tube. However, it has the greatest of all advantages, that of accuracy. The writer has used for some time a regular Bunsen furnace with a glass tube, and while the results were all that could be desired, the time required for a refractory residue was almost three hours.

A series of experiments was conducted with the ordinary chromic acid process, but the results were quite unsatisfactory. Every precaution was taken to insure accuracy, but with high carbon residue low results were obtained in nearly every case when checked by the oxygen combustion method. This was particularly noticeable when a considerable content of graphite was present. The results checked quite well with each other and gave satisfactory results when working on steel.

As this state of affairs greatly embarrassed matters in the laboratory, an effort was made to devise some means by which the carbon could be determined with reasonable speed and accuracy.

Recognizing the advantages of the combustion method, it was decided to make use of a platinum tube. To avoid delay and expense the tube was manufactured in the factory. It was made of 0.200 stock twelve inches long and eleven-sixteenths inch in diameter. A perfectly tight tube was constructed by using ordinary gold solder, which may be obtained from any jeweler. Around each end of the tube copper coolers were brazed, in order to cool the tube in the neighborhood of the rubber stoppers. The inlet of the coolers served the double purpose of supports and water supplies. In spite of this precaution it was found that the air circulating through the heated portion of the tube was hot enough, on reaching the stoppers, to seriously affect them. In order to prevent this, the scheme shown in Fig. 3

was devised. The funnel shape protuberance here seen was filled with ignited asbestos, and the whole was removed with the stoppers. This appliance proved an effectual preventive for further heating of the stoppers, as a red heat could be maintained two inches from them and they remain perfectly cool.

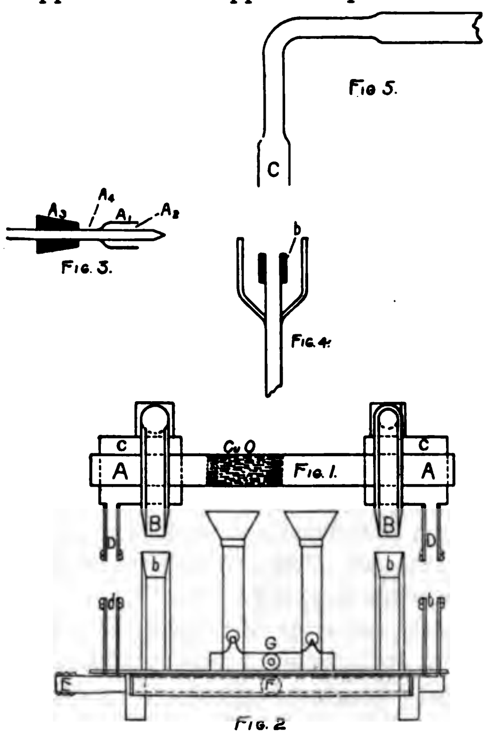


Fig. 1—*AA*, Platinum tube; *BB*, Support and water outlet; *CC*, Coolers; *DD*, Water supplies.

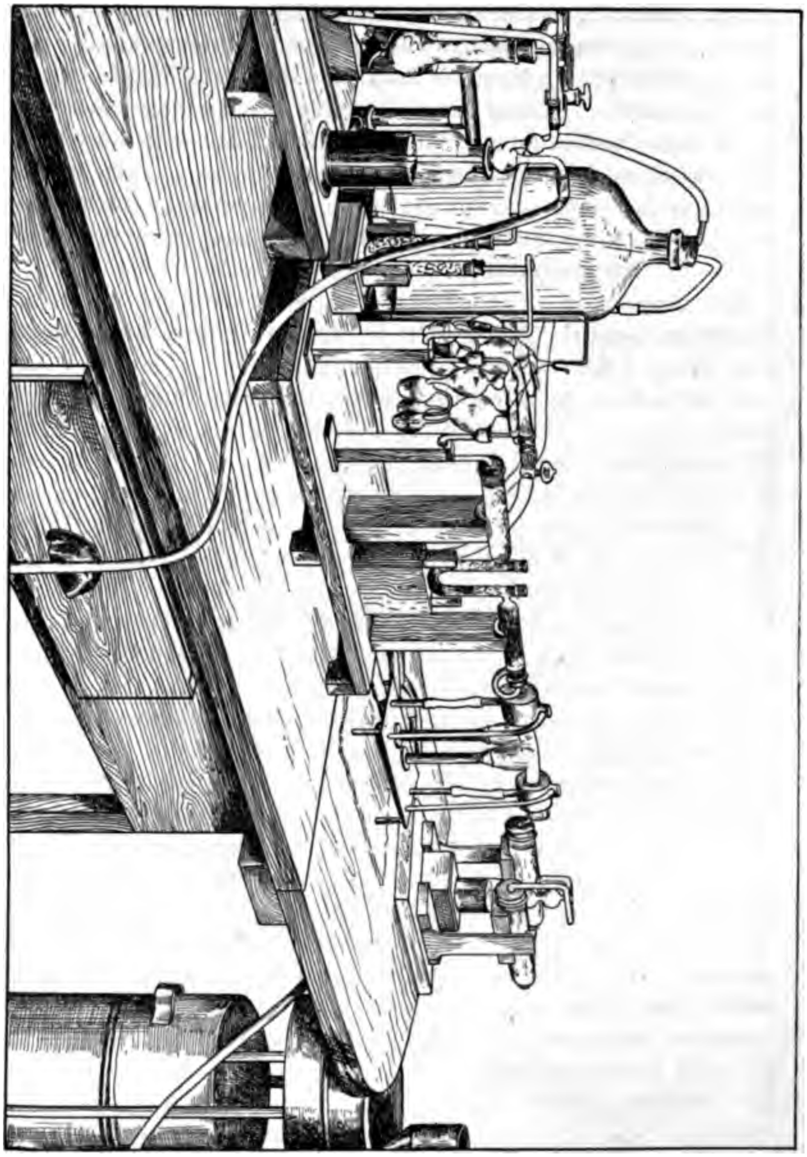
Fig. 2—*bb*, Sockets for *BB*; *dd*, Connection for water supply, *DD*: *E*, Main water supply; *F*, waste pipe; *G*, Gas connection.

Fig. 3—A_3, Stoppers; A_1, Glass cup for asbestos, A_2; A_4, Outlet.

Figs. 4 and 5—Showing connections for mercury joint.

With this arrangement it was found that a high carbon residue could be burned completely in twenty minutes. It became evident from this that if the aspirating space were decreased, good results could be obtained in a comparatively short time. With this idea in view, the train depicted in the accompanying picture was designed and made by our own glass-blowers. The train has the further advantage that rubber connections are avoided, the only rubber tubing in use being at the ends of the combustion tube.

The purifying train consists of a large U-tube of one and one-half inch stock and twelve inches long. The first limb is filled with broken caustic potash, and the second with fused calcium chloride. The first limb connects with a Drechsel bottle partially filled with strong sulphuric acid, and the second with the combustion tube.



The purifying train on the absorption end is made in one piece. It consists of a five inch U-tube of thick walled glass five-eighths inch in diameter, into the sides of the limbs of which are fused arms. These arms are made of one-inch stock and about seven inches long. The first arm is filled with anhydrous cuprous chloride and anhydrous cupric sulphate. The U-tube serves as the receptacle for the sulphuric acid, and the second arm is filled with calcium chloride previously treated with an excess of carbon dioxide.

The connection with the Geissler bulbs is established by means of mercury joints. These serve to facilitate removal of the bulbs and make a joint which is perfectly secure. The joint can readily be made by any glass blower, an illustration of which is seen in Fig. 4. The end of the Geissler bulb is so reamed as to fit loosely over the tube inside the cup (Fig. 5). A small piece of rubber tubing (*b*, Fig. 4) is slipped over the tube and makes a moderately tight joint with the end of the Geissler bulb. When the cup is filled with mercury a perfect connection is obtained. The method of connecting the Geissler bulb with rubber tubing was both awkward and liable to leakage. These junctions have been in use for some time in our laboratory and have given thorough satisfaction.

With this apparatus as described the most refractory residues are burned in an hour and a half. With residues of less refractory nature and lower carbon content an estimation may be completed in less time. The blank on the apparatus never exceeds three-tenths of a milligram, and is usually one-tenth or nil.

Some results are here appended, thinking they may be of interest. Those obtained by the chromic acid process were quite scattering unless great care was exercised and sufficient time was allowed. The results from this method, given below, are those where much time was given and great pains taken to insure complete oxidation. Values from the Bunsen furnace are given to serve for comparison.

Chromic Acid Method. Total Carbon.	Bunsen Furnace. Total Carbon.
3.23	3.31
3.27	3.33
3.23	...
3.28	...

Results from the above described process, when compared with the Bunsen furnace, were very good.

Platinum Furnace. Total Carbon.	Bunsen Furnace. Total Carbon.
3.03	3.03
3.03	3.05
3.05	...

The convenience of this apparatus in expediting work in the laboratory has led me to write this description, in the hope that it might be of service to other chemists.

CHEMICAL LABORATORY, WESTERN ELECTRIC COMPANY,
CHICAGO.

NOTE ON THE SOLUBILITY OF BISMUTH SULPHIDE IN ALKALINE SULPHIDES.

BY GEORGE C. STONE.

Received November 9, 1896.

IN the August number of this Journal there is a note by Prof. Stillman on this subject; he shows that if a solution containing bismuth is made alkaline by sodium hydroxide and then heated with an excess of an alkaline sulphide a considerable amount of bismuth is held in solution. On repeating his experiments qualitatively I obtained the same result, but when the bismuth was first precipitated as sulphide from an acid solution and then treated with an alkaline sulphide but little if any was dissolved.

To test the solubility quantitatively I made a solution of about one and two-tenths grams of bismuth hydroxide in 500 cc. of very dilute hydrochloric acid; in two portions, of fifty cc. each. I determined the bismuth by precipitation by ammonium carbonate, finding 0.0966 and 0.0965 gram.

I next precipitated the bismuth in two more lots of the same solution by hydrogen sulphide, filtered and heated the precipitate for half an hour with a large excess of potassium sulphide, filtered, dissolved and reprecipitated by ammonium carbonate, the bismuth weighed 0.0981 and 0.0970 gram.

Two more lots treated in the same manner, except that they were heated with ammonium sulphide, gave 0.0970 and 0.0976 gram of bismuth.

From the above it seems fair to conclude that bismuth sulphide precipitated from an acid solution is not dissolved by subsequent treatment with an alkaline sulphide.

[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY OF THE OHIO STATE UNIVERSITY.]

ON THE BEHAVIOR OF COAL-TAR COLORS TOWARD THE PROCESS OF DIGESTION.

BY H. A. WEBER.

Received October 10, 1896.

IT is very well known that the coal-tar colors have come into general use for coloring confectionery and other articles of food and drink. In fact they have almost completely superseded the vegetable colors, which have been used from time immemorial for a similar purpose. The indiscriminate use of these colors, some of which are derived from bodies of a decidedly poisonous nature, has often been regarded with suspicion by persons who are interested in public health. On account of the uncertainty existing in regard to these colors from a sanitary point of view, Austria has prohibited their use *in toto* in all articles of food and drink. Other countries prohibit certain of the colors, which have been shown to be injurious, and allow all others to be used.

The experiments made upon the lower animals have, in the main, revealed negative results. Thus the writer about eight years ago fed some of the colors most commonly employed by confectioners to rabbits in order to test this question. One-half gram of the colors, among which magenta and corallin were included, was fed to as many rabbits per day for ten days in succession without any apparent ill effects. The exhaustive treatise of Dr. Weil, translated by Leffmann, ascribes toxic effects to only a small number of the many colors employed by him in his experiments upon domestic animals.

The effect which these colors might exert upon digestive ferments, however, was a subject which had as yet received no attention, and the following experiments were undertaken in order to throw some light upon this question. The ferments employed were Armour's pepsin and pancreatine, liberal samples of which were kindly furnished by Armour & Co., of Chicago.

For the purpose of showing the digestive action, blood fibrin preserved in alcohol was employed. The fibrin was soaked and

thoroughly washed with water to remove the alcohol, then pressed between filter paper, and the amount required for each experiment weighed off.

In each set of experiments a control experiment was carried on without the addition of color. The mixture was made as follows:

Hydrochloric acid solution (two-tenths per cent.)	100 cc.
Pepsin......................................	20 milligrams.
Fibrin......................................	1 gram.

This mixture placed in a large test-tube was digested in a water-bath at a temperature of 38° to 40° C. until the fibrin was dissolved.

At the same time similar mixtures as above containing in addition 1, 0.5, 0.250, 0.125, and 0.062 gram of the color to be tested respectively, were digested in the same water-bath for the time required to dissolve the fibrin in the control experiment. Any fibrin remaining undissolved in the latter tests, was removed, thoroughly washed, pressed between filter paper as before and weighed.

1. PEPSIN AND OROLINE YELLOW.

This color was one of a series employed in the coloring of confectionery, and was found to be what is known in the trade as *Acid Yellow* or *Fast Yellow*, and is a mixture of sodium amidoazobenzenedisulphonate with sodium amidoazobenzenemonosulphonate.

	Amount of color. Gram	Amount of fibrin. Gram.	Amount of pepsin. Gram.	Duration of experiment. Hours.	Amouut of fibrın dissolved. Gram.
1	0.0	1	0.020	3	1.0
2	1.0	1	0.020	3	0.1
3	0.5	1	0.020	3	0.12
4	0.25	1	0.020	3	0.22
5	0.125	1	0.020	3	0.35
6	0.062	1	0.020	3	0.73

From this it will be seen that even in test No. 6, where the color employed amounted to only one part in 1600 parts of the solution, the presence of the color had still a depressing effect. For fear that, owing to the nature of this color, the hydrochloric acid might have been neutralized in part, the experiment was

repeated with a six-tenths per cent. solution of hydrochloric acid with similar results.

Of course the determination of the fibrin dissolved is only approximate, as can readily be inferred from the way it was done.

In tests Nos. 2, 3 and 4 no change in the amount of fibrin was apparent to the eye. That a small part of the fibrin had gone into solution was confirmed by the fact that a slight precipitate of albuminoids was obtained on the addition of a solution of tannin. On the whole it must be conceded that this color has a marked and injurious effect upon peptic digestion.

2. PEPSIN AND SAFFOLINE.

This is also a candy color and was found to be *acridine red.*

Amount of color. Gram.	Amount of fibrin. Gram.	Amount of pepsin. Gram.	Duration of experiment. Hours.	Amount of fibrin dissolved. Gram.
0.0	1	0.020	3½	1
1.0	1	0.020	5	1
0.5	1	0.020	5	1
0.25	1	0.020	5	1
0.125	1	0.020	3½	1
0.062	1	0.020	3½	1

As will be seen from the table above, this color only slightly retards the digestion of the fibrin in the three stronger solutions, while in the last two tests there was no interference with the process. On the whole it may be said that the effect of this color on peptic digestion is practically nil.

3. PEPSIN AND MAGENTA.

It is needless to tabulate the results of this experiment. Suffice it to say that the solution of the fibrin in the five tests containing the same proportions of the color as employed above kept pace throughout the whole duration of the experiment with the control test, the fibrin in all cases dissolving at the expiration of three and one-half hours.

This color, therefore, seems not to interfere with peptic digestion.

These four colors were also employed with pancreatin, and the method was as follows:

For the control experiment the following mixture was made :

Water	100 cc.
Sodium bicarbonate	1.5 grams.
Pancreatin	0.3 gram.
Fibrin	1.0 gram.

This mixture contained in a large test-tube, was digested in a water-bath until the fibrin was peptonized. To test the effect of the colors, there was added to similar mixtures as above 1, 0.5, 0.25, 0.125 and 0.062 gram of each color respectively.

5. PANCREATIN AND OROLINE YELLOW.

To the great surprise of the writer, this color, which had proved so effective in stopping and retarding peptic digestion, was found to exert no action whatever on the pancreatic ferment; the fibrin in all five of the tests with this color, dissolved as freely as that of the control test. The solution of the fibrin in all cases was completed at the expiration of six hours.

PANCREATIN AND SAFFOLINE.

The action of this color was quite different from that of oroline yellow, as the subjoined table will show :

	Amount of color. Gram.	Amount of fibrin. Gram.	Amount of Pancreatin. Gram.	Duration of experiment. Hours.	Amount of fibrin dissolved. Gram.
1	0.0	1	0.3	6½	1.0
2	1.0	1	0.3	6½	0.0
3	0.5	1	0.3	6½	0.0
4	0.25	1	0.3	6½	0.55
5	0.125	1	0.3	6½	0.65
6	0.062	1	0.3	6½	0.75

These results show, that in the two stronger solutions the action of the pancreatic ferment was entirely stopped, and that even in test No. 6, which contained only one part of color to 1600 of the solution the action of the ferment was retarded to a marked extent.

Tannin precipitates the coloring matter.

7. PANCREATINE AND MAGENTA.

This color was as marked in retarding and stopping the action of pancreatine as saffoline. The results are given in the table below :

	Amount of color. Gram.	Amount of fiber. Gram.	Amount of pancreatine. Gram.	Duration of experiment. Hour.	Amount of fiber dissolved. Gram.
1	0.0	1	0.3	6½	1.0
2	1.0	1	0.3	6½	0.0
3	0.5	1	0.3	6½	0.0
4	0.25	1	0.3	6½	0.40
5	0.125	1	0.3	6½	0.60
6	0.062	1	0.3	6½	0.73

The solutions of tests 2 and 3 gave no precipitate with tannin. In all other tests the precipitate was either marked or heavy.

8. PANCREATINE AND METHYL ORANGE.

This color in all of the tests behaved like the last three colors described, completely stopping the action of the pancreatine in the two strongest solutions and retarding it to a marked extent in the weakest. The tabular statement would be similar to the last.

It seems then, so far as these four colors are concerned, that none interfere with both peptic and pancreatic digestion, but that each color interferes seriously with either the one or the other. What the action of other coal tar colors may be, can, of course, not be inferred from this limited number of experiments, but it may safely be said that bodies which have such a decided action in retarding the most important functions of the animal economy, cannot properly have a place in our daily food and drink.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 19.]

THE ACTION OF ACID VAPORS ON METALLIC SULPHIDES.

BY JEROME KELLEY, JR. AND EDGAR F. SMITH.

Received October 2, 1896.

EXPERIMENTS made in this laboratory on the action of the vapors of hydrochloric acid upon the sulphide of arsenic proved that the latter is wholly volatilized. The purpose of the present communication is to record further observations along analogous lines. Thus, when washed and dried arsenic trisulphide is exposed to the action of hydrobromic acid gas, it volatilizes completely. Indeed the action commences in the cold with the formation of a liquid that passes out of the containing

vessel upon the application of a very gentle heat. In evidence of this, two quantitative experiments may be given:

Arsenic sulphide taken. Gram.	Arsenic sulphide expelled. Gram.
0.2945	0.2941
0.4632	0.4628

Antimony trisulphide, like that of arsenic, is volatilized by hydrochloric acid gas. It was quite probable that a like deportment would be observed if hydrobromic acid gas should be substituted. This was found to be the case. When the gas came in contact with the sulphide it became liquid and volatilized as soon as a gentle heat was played upon the boat in which the sulphide was contained.

Antimony sulphide taken. Gram.	Antimony sulphide expelled. Gram.
0.1473	0.1469
0.0938	0.0935

Upon substituting stannic sulphide for antimony sulphide, an experience similar to that observed with antimony and arsenic sulphides followed. There was a complete volatilization with but a trifling residue, which proved to be carbon from filter paper that had adhered to the metallic sulphide.

Stannic sulphide taken. Gram.	Stannic sulphide expelled. Gram.
0.1880	0.1880
0.5527	0.5521
0.4174	0.4169

The oxides of arsenic, antimony and tin (at least in the stannic form) can be volatilized in a current of hydrochloric acid gas. This is also true of the sulphides of arsenic and antimony, but how the two sulphides of tin would act under like conditions was not known.

Experiments recently made demonstrate the perfect volatility of stannic sulphide in this way. With stannous sulphide it was found that by the continued action of the gas in the cold there followed a complete conversion into chloride without any volatilization. That the residue was the chloride was evident from its action upon a mercuric salt solution. The figures obtained in the several trials were:

Stannous chloride found. Gram.	Stannous chloride theory. Gram.
0.3544	0.3523
0.4893	0.4903

Several attempts were made to separate stannous and stannic sulphides by this procedure. The results were unsatisfactory. In order to drive out the stannic salt completely it is necessary to heat the mixture, and this caused a partial volatilization of the stannous chloride, so that quantitative results could not be obtained.

Comparatively few metallic sulphides have been studied in the direction indicated in the preceding lines, so that it is probable a wider application of the method will disclose interesting behaviors, and that probably new separations can be brought about in this way. The action of the vapors of haloid acids has also been tried on natural sulphides with a fair degree of success.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 20.]

TUNGSTEN HEXABROMIDE.

BY HERBERT A. SCHAFFER AND EDGAR F. SMITH.

Received October 10, 1896.

THE most recent work upon tungsten bromides is that of Roscoe,[1] who endeavored to prepare a hexabromide, but obtained instead a penta derivative from which the dibromide was subsequently made. By reference to the literature bearing upon this subject it will be noticed that bromine, diluted with carbon dioxide, was made to act upon tungsten metal exposed to a red heat. Experimental evidence is at hand that tungsten at high temperatures deoxidizes carbon dioxide, thus allowing ample opportunity for the production of oxybromides, which, in spite of the greatest care, are sure to appear in larger or smaller amount. The thought also suggested itself that possibly the "red heat" at which the action was allowed to occur might have been detrimental and have indeed prevented the formation of the hexabromide.

Hence, we determined to operate in an atmosphere of nitro-

[1] *Ann. Chem.* (Liebig), 162, 362.

gen and to apply a very gentle heat to the vessel containing the tungsten. In this connection it may be mentioned that the nitrogen was conducted through a series of vessels charged with chromous acetate, sulphuric acid, caustic potash, and phosphorus pentoxide, respectively. It then entered an empty vessel into which dry bromine was dropped from a tap-funnel, and after passing through a tall tower, filled with calcium chloride, entered a combustion tube resting in a Bunsen furnace. The anterior portion of the combustion tube was contracted at intervals, forming a series of bulbs, and at its extremity was connected with an empty Woulff bottle, followed by a calcium chloride tower, and finally a receiver filled with soda lime and broken glass. A steady current of nitrogen was conducted through this system for a period of three days. On the fourth day bromine was introduced. The tungsten contained in the combustion tube was heated very gently. In a short time brown vapors appeared. These condensed to a liquid beyond the boat and eventually passed into blue-black crystalline masses that separated from the walls of the tube, when perfectly cold, with a crackling sound. Very little heat was required to melt them and they could with care be resublimed in distinct, blue-black needles. The latter was collected in one of the bulbs (No. 2) previously mentioned. Other products were observed and isolated. All were analyzed. Bulb No. 1—that nearest the tungsten metal—contained a black, velvety compound, which upon analysis showed the presence of tungsten dibromide. Bulb No. 2 contained 0.2103 gram of the blue-black crystals, which yielded 0.0577 gram of tungsten, or 27.43 per cent., and 0.1543 gram of bromine, or 73.53 per cent. The theoretical requirements of tungsten hexabromide are 27.72 per cent. tungsten and 72.28 per cent. bromine. The bromine percentage found is high. This may be due to traces of bromine that had not been driven out from the crystalline deposit, or to adherent silver tungstate, as some tungstic acid remained in the solution from which the silver bromide was precipitated.

A fresh portion of the blue-black crystals was prepared as before and analyzed. The bromine determination was unfortunately lost. The determination of the tungsten resulted as fol-

lows: 0.4351 gram of material gave 0.1222 gram of tungsten or 28.08 per cent.

A third preparation was made. On subjecting 0.1775 gram of it to analysis these results were obtained:

0.0496 gram tungsten or 27.94 per cent.

0.1266 gram bromine or 71.32 per cent.

Tabulating the series, we have:

	Found.			Mean	Required for hexabromide.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Tungsten......	27.43	28.08	27.94	27.81	27.72
Bromine.......	73.53	71.32	....	72.33	72.28

These figures give evidence that the body analyzed is tungsten hexabromide.

In analyzing the third portion of the blue-black needles the bromine was determined by placing the material in a small Erlenmeyer bulb, covering it with nitric acid and then distilling. The liberated bromine was passed into a silver nitrate solution.

The tungsten hexabromide prepared by us consists, as already observed, of blue-black needles. Moderately elevated temperatures decompose the compound. It gives off fumes when brought in contact with the air. Water decomposes it with the formation of a royal-blue colored oxide. Ammonia water dissolves it, the solution remaining colorless. A vapor density determination resulted negatively, as decomposition was apparent early in the experiment.

NOTES ON THE FERROCYANIDES OF ZINC AND MANGANESE.

By Edmund H. Miller.

Received October 10, 1896.

THE composition of the ferrocyanides of zinc and manganese, formed when salts of these metals are precipitated by potassium ferrocyanide, is given by Prescott and Johnson[1] as $Zn_2Fe(CN)_6$ and $Mn_2Fe(CN)_6$, while the books on volumetric analysis, such as Sutton's and Beringer's, ignore the composition of this precipitate.

[1] Qualitative Analysis, pages 67 and 57.

The prevailing idea is that in the titration of zinc by potassium ferrocyanide, a normal zinc ferrocyanide is formed. This I believe to be incorrect, for if the reaction is

$$K_4Fe(CN)_6 + 2ZnCl_2 = Zn_2Fe(CN)_6 + 4KCl,$$

a solution of potassium ferrocyanide, one cc. of which is equivalent to ten milligrams of zinc, would contain 32.32 grams of $K_4Fe(CN)_6.3H_2O$ to the liter, not 43.2[1] to 45[2] grams, as has been found by experiment. Using forty-four grams per liter as a basis for calculation, the reaction becomes

$$2K_4Fe(CN)_6 + 3ZnCl_2 = Zn_3K_2(Fe(CN)_6)_2 + 6KCl.$$

This reaction is not merely one that may possibly be true, but according to Wyrouboff,[3] the precipitate formed by the action of potassium ferrocyanide on a zinc salt, whichever is in excess, is $3Zn_2Fe(CN)_6.K_4F_2(CN)_6.12H_2O$, white, while the normal salt, $Zn_2Fe(CN)_6.4H_2O$, is formed only by the action of hydroferrocyanic acid on a zinc salt.

This statement agrees both with the preceding reaction and with the results obtained in standardizing potassium ferrocyanide solution.

The manganese precipitate with potassium ferrocyanide, as obtained in titration, is given by Stone[4] as $Mn_3Fe_2(CN)_{12}$. This is a ferri-, not a ferrocyanide, thus making necessary a change of quantivalence. Mr. Stone also states that an amount of potassium ferrocyanide which will precipitate four atoms of zinc will only precipitate three of manganese, thus basing his calculation on the formation of a normal zinc ferrocyanide.

Wyrouboff[1] gives the precipitate obtained from potassium ferrocyanide and a manganese salt, whichever is in excess, as

$$5Mn_2Fe(CN)_6.4K_4Fe(CN)_6.4H_2O, \text{ rose white };$$

while the normal salt $Mn_2Fe(CN)_6.7H_2O$, cream, is formed as in the case of zinc by hydroferrocyanic acid.

The solution used by Mr. Stone had the following strength :

[1] Sutton: Volumetric Analysis, p. 329; Beringer: Assaying, p. 219.

[2] Furman: Assaying, p. 205.

[3] *Ann. chim. phys.*, [5], 8, 485.

[4] *J. Am. Chem. Soc.*, 17, 473.

One cc. = 0.00606 gram zinc.
One cc. = 0.00384 gram manganese.

If the ratio were exactly four zinc to three manganese, using the most recent atomic weights, the strength of this solution against manganese would be one cc. = 0.00382 gram, while, according to Wyrouboff,[1] $10Mn = 9K_4Fe(CN)_6$ and $6Zn = 4K_4Fe(CN)_6$, or $10Mn = 13.5 Zn$, or $1 Mn = 1.35 Zn$, and the strength against manganese would be 1 cc. = 0.003774 gram.

These figures show but little difference between the two ratios and while Mr. Stone's experimental results are undoubtedly accurate, this theory based on the formation of $Zn_2Fe(CN)_6$ and $Mn_3Fe_2(CN)_{12}$ is not satisfactorily proved.

This article is only a preliminary note regarding the composition of the ferrocyanides as they are being investigated in this laboratory.

In connection with the ferrocyanide of zinc I have found a very strong solution of hydrochloroplatinic acid, H_2PtCl_6, acidified with hydrochloric acid, a most satisfactory indicator for the titration of zinc by potassium ferrocyanide, when performed in a hot solution. This indicator is used in the same way as uranium acetate and is less affected by a varying amount of hydrochloric acid. The end reaction is a bright emerald green, which takes a few seconds to develop. It will not work with a cold solution.

ASSAY LABORATORY, COLUMBIA UNIVERSITY.

A MODIFICATION OF THE GUNNING METHOD FOR NITRATES.

BY JOHN FIELDS.

Received October 20, 1896.

THE full text of the official Gunning[2] method is as follows: "In a digestion flask, holding from 250 to 500 cc., place from seven-tenths to three and five-tenths grams of the substance to be analyzed, according to the amount of nitrogen present. Add thirty to thirty-five cc. of salicylic acid mixture; namely, thirty cc. sulphuric acid to one gram of salicylic acid, shake until thoroughly mixed and allow to stand five to ten

[1] *Ann. chim. phys.*, [5], 8, 474.
[2] Bulletin 46, U. S. Dept. of Agr., p. 18.

minutes, with frequent shaking; then add five grams sodium thiosulphate and ten grams of potassium sulphate. Heat very gently until frothing ceases, then heat strongly until nearly colorless. Dilute, neutralize, and distil as in the Gunning method."

This method has its advantages in that no heavy metals are added, such as zinc and mercury, which sometimes interfere with the distillation. It has, however, a few disadvantages which the following modification partially overcomes. When working with some materials, there is considerable trouble due to persistent frothing, and in some cases, it has taken six hours constant attention to get the digestion safely over this point. Moreover, unless the contents of the flask are diluted while still warm, there is a tendency for the sulphates to become hard and difficult of solution.

In the modification proposed, the following reagents are necessary:

1. Chemically pure sulphuric acid.
2. Salicylic acid.
3. Potassium sulphide.

The material containing the nitrates is weighed out into a digestion flask and thirty cc. sulphuric acid containing one gram salicylic acid are added, and gently heated to facilitate the solution of nitrates and prevent frothing later. While warm, six to seven grams of potassium sulphide are added in small portions, the flask being thoroughly shaken after each addition. It is then placed over a low flame and the heat rapidly increased until the acid mixture boils. No further attention is required and the digestion is usually complete at the end of an hour. When cold, the liquid is diluted and distilled in the usual manner.

The average difference between the results on sixty samples of fertilizers containing nitrates by the official method and the proposed modification was 0.02 per cent., those by the latter being higher.

The points of difference between the modification and the official modified Gunning are the following:

1. The number of reagents used in the digestion is reduced from four to three.

2. Frothing is obviated and the operation requires no attention except turning up the lamps until full heat is secured.

3. The time of digestion is shortened.

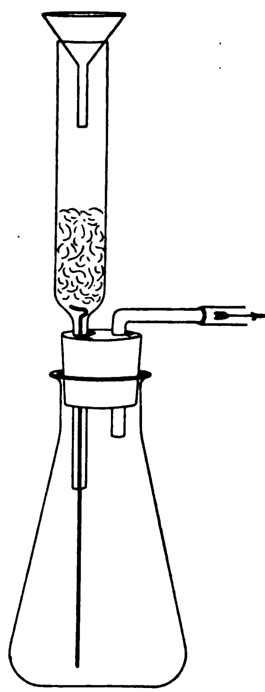
4. Potassium sulphide is made to do double work by acting as a reducing agent instead of sodium thiosulphate and then being converted into potassium hydrogen sulphate serving the end secured by adding potassium sulphate in the original method.

THE SEPARATION OF ALKALOIDAL EXTRACTS.

BY CHARLES PLATT.

Received October 20, 1896.

THE writer has found the accompanying simple device of great value in the separation of the annoying emulsions so often met with in alkaloidal analysis, as, for instance, in the petroleum ether and benzene extractions of Dragendorff's method. The filtering tube is nineteen cm. long, the upper 12.5 cm. having an inside diameter of fourteen mm., the lower contracted portion, an inside diameter of three mm. A stout platinum wire bent at the upper end is so placed as to pass through the constricted portion of the tube to the bottom of the eight-ounce Erlenmeyer flask. Washed cotton is firmly packed in the tube to a depth of about four cm. and the apparatus, connected with a filter pump, is ready for use. The filtered liquids may finally be carefully poured into an ordinary separating funnel and manipulated as usual. By this method the most persistent emulsions are separated into their constituent liquids in as many minutes as ordinarily are required hours or days.



CHEMICAL LABORATORY, HAHNEMANN MEDICAL COLLEGE,
PHILADELPHIA, PA.

THE PREPARATION OF DIETHYL MALONIC ESTER.

By W. A. Noyes.

Received October 29, 1896.

HAVING occasion recently to prepare considerable quantities of malonic ester, it has been found that the process can be very much shortened by the use of sulphuric in place of hydrochloric acid and of acid sodium carbonate in place of potassium carbonate. As the body is the starting point for a great variety of syntheses the method used may be of interest to others.

One hundred grams of chloracetic acid are placed in a porcelain dish, 21 cm. in diameter, and 200 cc. of water added. The solution is warmed and ninety grams of acid sodium carbonate added in small portions, and the warming continued until a temperature of 55°–60° is reached and effervescence nearly ceases. Eighty grams of coarsely powdered potassium cyanide is then added, and the whole stirred without further warming, till the somewhat vigorous reaction is complete. The solution is then evaporated rapidly on a thin sheet of asbestos paper till the thermometer with which it is vigorously and constantly stirred shows a temperature of 130°–135°. The hand should be protected by a glove or otherwise, and the glass of the hood in which the evaporation is conducted should be between the dish and the face during this part of the process. The mass should be stirred occasionally while cooling, and as soon as it solidifies it should be broken up coarsely and transferred to a liter flask. Add forty cc. of alcohol and connect with an upright condenser. Through the latter add, in small portions and with frequent shaking, a cooled mixture of 160 cc. of alcohol with 160 cc. of concentrated sulphuric acid. The whole may be added within five or ten minutes (instead of the day and a half required to saturate with hydrochloric acid by the old method). Toward the close there is a considerable evolution of hydrochloric acid. Heat on a water-bath for an hour. Cool quickly under the tap, with shaking to prevent the formation of a solid mass of crystals. Add 200 cc. of water, filter, wash the undissolved salts with about fifty cc. of ether, shake up with the filtrate and separate. Add a solution of sodium carbonate and shake carefully

with the ethereal solution till alkaline. Separate again, distil off the ether and dry by heating for fifteen minutes on a water-bath under diminished pressure, using a capillary tube as for vacuum distillations. The residue gives, after one distillation, an almost pure malonic ester.

The sodium carbonate solution appears to contain some of the acid ester. If this solution is added to the first acid solution, the ester separates with some ether. The ethereal solution may be separated, the ether evaporated at a gentle heat, and the residue added to the contents of the flask in which a second saponification of the cyanacetate is to be effected. If this is done, a yield of malonic ester equal to the weight of chloracetic acid used can be obtained. This is ten to fifteen per cent. better than by the old method.

ROSE POLYTECHNIC INSTITUTE,
TERRE HAUTE, IND., Oct. 27, 1896.

NOTE.

Untaxed Alcohol for Use in Manufacturing and in the Arts.—The Joint Select Committee, created at the last session of Congress, to investigate and report upon the question of the use of alcohol free of tax in the manufactures and arts, have prepared a series of interrogatories, which will be distributed throughout the country to such parties as are thought to be interested in the question.

The report of Mr. Henry Dalley, Jr., who was commissioned to investigate the workings of foreign laws governing the use of untaxed alcohol in the manufactures and arts has been submitted, and contains very full and extremely valuable data covering Great Britain, Germany, France, Belgium and Switzerland.

It is the earnest desire of the committee to secure all possible information bearing upon the subject, and it is hoped that parties interested will submit their views to the committee promptly. Sets of the circular letter and blank for replies will be supplied to any applicant by addressing the chairman, Room 21, Senate Annex, Washington, D. C.

The committee, which is composed of three members of each House, will probably assemble in Washington soon after the

middle of November for the purpose of formulating a report to Congress accompanied by the draft of a law which will place domestic industries on as favorable a basis as similar industries in foreign countries. During their sessions in Washington hearings will probably be given in order to supplement the information obtained through the interrogatories above set forth. Due notice of the time of such hearings will be given to the public.

OBITUARY NOTICE.

PROFESSOR AUGUST KEKULÉ'S part in the advancement of chemistry has been so important that his death on the 13th of last July has brought a feeling of sorrow to the hearts of chemists throughout the world.

Kekulé was born at Darmstadt, the birthplace of Liebig, on the 7th of September, 1829. It was the intention of his parents that he should become an architect, and he entered the University at Giessen as a student of architecture. He devoted himself with application to the studies bearing on his future calling, but like many another student who came within the range of Liebig's influence, he was filled with an enthusiasm for chemistry, which changed all his plans for the future, and led him to devote himself to this science. It is quite possible that his preliminary architectural studies had much to do with turning his mind toward the ideas of molecular structure or molecular architecture, which he subsequently developed. Kekulé also studied in Paris under Dumas, and in London under Williamson. In 1856 he became privatdocent at the University of Heidelberg. He was appointed professor of chemistry at the University of Ghent (Belgium) in 1858; and in 1865 was called to the University of Bonn, where he remained until his death.

Kekulé's first published work appeared in Liebig's *Annalen* for 1850. Four years later he published his second paper, in which he described thiacetic acid and discussed the action of phosphorus pentasulphide on oxygen acids.

The period from 1854 to 1874 was one of the greatest activity with Kekulé. Since 1874 he has made comparatively few con-

tributions to chemistry, although occasional papers have appeared. In spite of the great number of investigations he has made, chemistry is most indebted to Kekulé for his great generalizations and theoretical suggestions.

He extended Gerhardt's type theory by adding the marsh gas type and introducing the idea of mixed types. These types made clear to him the difference in the power of the elements to hold other atoms in combination, and he developed the idea of valence, first put forward by Frankland, so that this new property of the elements was at once recognized by chemists, the conception of atom-linking followed at once, and this made possible the transition from the type theory to our present conceptions in regard to the structure of compounds.

In this paper published in 1858 Kekulé says: "It is the substitution and relation of the atoms and not radicals, that we must look to in order to get a clearer idea of the nature of these compounds."

He closes this remarkable paper with the following words: "In conclusion I believe that I should emphasize that I do not set much value upon this kind of speculation. But since chemistry, in its entire lack of exact scientific principles, must content itself for the time with the most probable and useful theories; it appears proper to present these views, for they, as it seems to me, give a simple and entirely general expression for the latest discoveries, and because moreover their application may be the means of discovering new facts."

It is not too much to say that the ideas thus modestly put forward, supported by his subsequent work, were the prime cause which led to the abandoning of Gerhardt's types for our present structural formulas.

These ideas had made considerable progress, when in 1865 Kekulé published his now well known hypothesis in regard to the constitution of benzene. Seldom has a theory in chemistry been so suggestive or given rise to so much investigation as this benzene theory. The rich and manifest results accruing from these investigations testify sufficiently to the utility of the theory.

Many students of chemistry were attracted to Bonn; these Kekulé inspired with a love of investigation that has been

exceedingly fruitful for the science. Besides his work as a lecturer and investigator, he began in 1860 and finished in 1861 the first volume of his *Lehrbuch der organischen Chemie*, a book that was epoch-making with its new ideas and new methods of presenting this complex subject. The book was received with enthusiasm among chemists, and has served as a model for subsequent works in the same field. Three volumes of this work were finally published, but the work was never completed. He was also for many years one of the editors of Liebig's *Annalen*. During his last years he suffered much from ill health, having followed too literally Liebig's advice: "If you would become a chemist, you must ruin your health. He who does not ruin his health by hard study in these days comes to naught in chemistry."

In 1890 the German Chemical Society celebrated the twenty-fifth anniversary of Kekulé's benzene theory. The meeting was largely attended by chemists from all parts of the world. Addresses were given by A. W. Hofmann, the President of the Society, Adolph von Baeyer, Kekulé's oldest pupil, and by Kekulé himself. A full account of the meeting has been published.[1] G. M. RICHARDSON.

OCT. 17, 1896.

NEW BOOKS.

MANUAL OF DETERMINATIVE MINERALOGY WITH AN INTRODUCTION ON BLOWPIPE ANALYSIS. By George J. Brush. Revised and Enlarged by Samuel L. Penfield. 14th Edition. pp. ix + 108. John Wiley & Sons. Price, $3.50.

This revision, with the exception of the tables, is practically a new book. The author states that "A complete revision of the tables for the determination of minerals will be made as soon as possible, and a short chapter on crystallography and the physical properties of minerals will be prepared, but until this work can be accomplished, use will be made of the tables and of the short introduction to them from the last edition of Professor Brush."

This proposed revision of von Kobell's table is greatly needed. When it is finished the book bids fair to be as nearly perfect as text-books can well be. The introductory chapter has been rewritten with evident care and by a practiced hand, and as it

[1] *Ber. d. chem. Ges.*, 23, 1265.

now stands this edition is a great improvement over preceding ones.

"In preparing the introductory chapters, great pains have been taken in the selection of the tests for the elements. Many of them are performed by means of the blowpipe, but chemical tests in the wet way are recommended when it is believed that they are more decisive." To this evidence of good common sense it may be added that in several places the author shows a desire and ability to make his knowledge of practical value. This is shown, for example, under gold, where careful directions are given for the detection of gold in poor gold ores and the like, first by the use of mercury and then without mercury. E. H.

THE ELEMENTS OF CHEMISTRY. By PAUL C. FREER, PH.D. x+284 pp. Boston: ALLYN & BACON. 1895. Introductory price, $1.00.

One feature in particular makes this book especially worth noticing, and that is its outright recognition of the great importance of quantitative work in an elementary course in chemistry. The recognition has been a long time on the way, and its absence has been a great detriment to the chemical instruction in secondary schools.

It is also pleasant to find Professor Freer recognizing that certain so-called physical matters are best reviewed at the outset of such a course. Indeed it would seem as if some such matters which are taken up in the present work, rather late in the course, would better be considered earlier (the laws of Mariotte and Charles for instance).

The book cannot be used to advantage by an inadequately trained teacher, but will certainly be found valuable to the student teacher on account of its excellent collection of experiments which are carefully planned and digested.

JOSEPH TORREY, JR.

TABLES AND DIRECTIONS FOR QUALITATIVE CHEMICAL ANALYSIS. By M. M. PATTISON MUIR.

This little work is evidently intended to increase the possibilities of lecture table instruction in qualitative analysis. It consists of such brief statements of processes and methods as will enable the student to attend to what is going on on the lecture table without running the risk of losing material which ought to get into his note book. The analytical methods described are, for the most part, such as have stood the test of time and experience. JOSEPH TORREY, JR.

THE LIQUEFACTION OF GASES. Papers by MICHAEL FARADAY, F.R.S. (1823–1845). Alembic Club Reprints No. 12. 79 pp. Edinburgh: WM. F. CLAY. Price, two shillings.

In this little book of seventy-nine pages there is much matter

that will be of practical service to every one who teaches elementary chemistry. Its value to investigators and advanced students is sufficiently obvious. Students ought to be introduced to the classics of chemistry at a comparatively early stage of their development. They are not as a rule, at present, because the original papers are seldom accessible to the teacher. The publication of Ostwald's "Klassiker" was the first step in the right direction, but the fact that they are in German makes them inaccessible to many who most need them.

JOSEPH TORREY, JR.

CORRESPONDENCE.

POLARIZATION BY DOUBLE DILUTION.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., Nov. 27, 1896.

Editor Journal of the American Chemical Society, Easton, Pa.:

DEAR SIR: By accident a portion of the rule for calculating polarizations by double dilution in our paper published in this Journal, 1896, Vol. 18, pages 428 to 433, was omitted.

Page 430, beginning at the end of line 9, the rule for the approximate calculation of results obtained by Scheibler's method of double dilution should have this addition after the words "small flask," "multiply the difference by two and subtract the product from the reading in the small flask." This is equivalent to multiplying the reading obtained from the solution in the large flask by four and subtracting the reading obtained from the solution in the small flask from the product. The result is the corrected reading and, when a solution of double the normal strength is polarized in a tube of double the normal length, must be divided by four to obtain the percentage. In this case a simpler and equivalent rule for calculation is the following: Subtract one-fourth the reading of the solution in the small flask from the reading in the large flask and the result will be the corrected percentage.

Page 430, end of line 17, the word sucrose should be lactose.

Page 432, the figures in the table in the column headed "Vol-

ume of precipitate," were calculated before the exact formula on page 430 was evolved, and are somewhat at variance with the results obtained by use of the formula. The formula gives the following numbers: 5.26, 10.71, 4.88, 9.86, 5.05, 5.41, 4.53, 4.12, 3.87, 4.99, 3.33, 4.22, 16.23. The numbers in the column headed "True volume in 100 cc. flask" must be changed accordingly.

Respectfully,

H. W. WILEY,
E. E. EWELL.

BOOKS RECEIVED.

Bulletin No. 33. Commercial Fertilizers and Chemicals, and Other Information in Regard to Fertilizers. Under the supervision of Hon. R. T. Nesbitt, Commissioner of Agriculture of the State of Georgia. Dr. George F. Payne, State Chemist. Atlanta, Ga.: George W. Harrison, State Printer.

Manual of Determinative Mineralogy, with an Introduction on Blowpipe Analysis. By George J. Brush. Revised and enlarged by Samuel L. Penfield. Fourteenth Edition. x+ 108 pp. New York: John Wiley & Sons. Price $3.50.

Jahrbuch der organischen Chemie. Herausgegaben von Gaetano Minunni. Palermo. Zweiter Jahrgang. 992 pp. 1894. Leipzig: Johann Ambrosius Barth. (Arthur Meiner). 1896.

A Brief Introduction to Qualitative Analysis; for Use in Instruction in Chemical Laboratories. By Ludwig Medicus. Translated from the Fourth and Fifth German Editions by John Marshall. Fourth Edition. Philadelphia: Printed by J. B. Lippincott Co. 1896. 203 pp. Price $1.50.

Bulletin No. 43. Second Series. Bovine Tuberculosis in North Louisiana. Bulletin of the Louisiana State Experiment Station, Baton Rouge, La. 1896. 20 pp.

ERRATUM.

On page 994 (November number), seventh line from bottom, instead of "extra internal pressure" read "extra external pressure."

Index to Vol. XVIII, 1896.

References to the pages of the Proceedings are given in Parenthesis.

Issued with January Number, 1896.

Proceedings.

BOARD OF DIRECTORS.

The Board of Directors have passed the following resolutions:

"*Resolved*, That the Board of Directors hereby approve and ratify the action of the majority of said Board, as obtained by their signatures, in granting a charter for a Local Section of the American Chemical Society in North Carolina, and that the charter date from the time said action was taken, November 8, 1895."

"*Resolved*, That the Finance Committee of the American Chemical Society is hereby authorized to approve, and the treasurer to pay to the General Secretary each month during the year 1896 a bill or bills for clerical help, provided, however, that the total sum called for by said bills does not amount to two hundred and fifty dollars ($250.00)."

NEW MEMBERS ELECTED NOVEMBER 21, 1895.

Bailey, Ralph Waldo, Elizabeth, N. J.
Bischoff, Dr. Ernst, 87-89 Park Place, New York City.
Broadhurst, W. Homer, Polytechnic Inst., Brooklyn, N. Y.
Doerflinger, Wm. F., Polytechnic Inst., Brooklyn, N. Y.
Holbrook, Frederick A., 75 Joralemon St., Brooklyn, N. Y.
Jameson, A. H., Cleveland Linseed Oil Co., S. Chicago, Ill.
Le Boutillier, Clement, High Bridge, N. J.
Morgan, J. Livingston Rutgers, New Brunswick, N. J.
Perry, Frank J., B.S., Polytechnic Inst., Brooklyn, N. Y.
Potter, Charles A., 174 Weybosset St., Providence, R. I.
Shaw, Wm. T., Chem. Lab. Agr. Exp. Sta., Bozeman, Mont.
Tucker, S. A., 135 Madison Ave., N. Y. City.
Tyrer, Thomas, Stirling Chem. Works, Stratford, E., England.

ASSOCIATES ELECTED NOVEMBER 21, 1895.

Tuckerman, Alfred, 342 West 57th St., N. Y. City.

NEW MEMBERS ELECTED DECEMBER 13, 1895.

Bellam, Henry Lynch, B.S., Anaconda, Mont.
Cameron, Prof. Frank Kenneth, Catholic Univ. of America, Washington, D. C.

Cushman, Allerton S., Washington Univ., St. Louis, Mo.
Cutts, Henry E., care Stillwell & Gladding, 55 Fulton St., N. Y.
Elliott, E. C., care Univ. of Nebraska, Lincoln, Nebr.
Hobbs, Perry L., Western Reserve Medical College, Cleveland, Ohio.
Meisel, C. F. A., 402 Washington St., New York City.
Moore, Chas. C., Jr., Dept. Agr., Div. Chemistry, Washington, D. C.
Schmidt, H. B., 215 E. 4th St., Cincinnati, Ohio.
Stoddard, Dr. H. T., 57 Crescent St., Northampton, Mass.
Thomas, W. S., Belt, Cascade Co., Mont.

ASSOCIATE ELECTED DECEMBER 13, 1895.

Waldman, Louis I., P. O. Box 162, Albany, N. Y.

CHANGES OF ADDRESS.

Appleton, Prof. J. H., 209 Angell St., Providence, R. I.
Benton, Geo. W., 27 E. St. Joe St., Indianapolis, Ind.
Dalton, Parmly, Swampscott, Mass.
Dunham, E. K., 338 E. 26th St., New York City.
Ehrenfeld, A. Clemens, Steele High School, Dayton, O.
Feid, George F., 519 Findlay St., Cincinnati, Ohio.
Griffith, Dr. S. H., U. S. Naval Museum of Hygiene, Washington, D. C.
Guiterman, Franklin, care Omaha and Grant Sm. Co., Durango, Colo.
Hewitt, Edward R., 119 E. 18th St., New York City.
Lammers, Theodore L., Helena, Mont.
Textor, Oscar, 158 Superior St., Cleveland, Ohio.
Trubek, M., Raceland, La.
Volckening, Gustave J., 88 Clinton Ave., Brooklyn, N. Y.
Wood, Edward, Harvard Medical School, Boston, Mass.

ADDRESS WANTED.

Grosvenor, Wm., Jr., Last address, Box 166, Johns Hopkins Univ., Baltimore, Md.

MEETINGS OF THE SECTIONS.

NEW YORK SECTION.

The regular meeting was called to order December 6th, 1895, at 8.25, Prof. P. T. Austen in the chair. There were about sixty members present.

The chairman opened the meeting with the statement that Dr. Webb, the President of the College of the City of New York,

and Prof. R. Ogden Doremus, had put the chemical lecture room of the college at the disposal of the society; and in his opinion it was the most satisfactory and most favorably situated of any that had yet been considered. He then introduced Prof. Doremus, who said that he was as much surprised as any one at the success of the society's request, as he had been under the impression that there was something in the charter of the college which prevented such use of the room. He remarked that the laboratory was now, since the destruction of the University building, the oldest educational chemical laboratory in the city.

He hoped the society would find it suitable to their purpose and assured it of the heartiest welcome.

The minutes were then read and the remarks of Prof. McMurtrie in regard to Illinois waters, as reported, were corrected, and the minutes adopted. Prof. McMurtrie moved that the thanks of the Section be sent to President Webb and Dr. Doremus for their courtesy in giving the Section the use of the lecture room. The motion was seconded and carried.

A letter addressed to the chairman from the Secretary of the English Society of Chemical Industry was then read, thanking the New York Section and the Lehigh Valley Section of the American Chemical Society, and the New York Section of the Society of Chemical Industry for the honor done to the President of their Society, Mr. Thos. Tyrer, and the Hon. Foreign Secretary, Mr. Ludwig Mond, on the occasion of their recent visit to New York.

The letter was ordered on file.

Prof. Moale read a paper entitled "A Brief History of Naphthalene," in which the work of the earliest investigators of this interesting substance as well as those in recent years, was reviewed.

Mr. Neiman was called upon by the chairman and gave his experiences in attempting to make naphthalene synthetically, for the purpose of deciding its theoretical constitution.

He stated that the decomposition of certain amido-naphthol-sulpho-acids having a tendency to show that the position of the double bonds in the naphthalene ring are not symmetrical, attempts were made to disprove this by the synthetic production

of naphthalene from ortho-xylene tetrabromide and ethane. By passing ethane over a heated mixture of granulated pumice stone and ortho-xylene tetrabromide, a portion of naphthalene was formed, but circumstances prevented the further investigation in this line. This formation would seem to show that the central bond is a double one, and the formula a symmetrical one as far as the bonds are concerned.

The second paper of the evening, on "Vegetable Proteids," was read by the author, Dr. T. B. Osborne.

Mr. Hewitt asked if a ten per cent. solution of sodium hydroxide would extract all the proteids or only one, or only a few.

Dr. Osborne replied that all the proteids would dissolve.

Mr. Hewitt had extracted the white bean in large quantities, agitating the bean flour in dilute alkali by machinery, and had obtained a clear solution which filtered readily.

Mr. Hewett asked if there was any difference in the product on repeated precipitations. Dr. Osborne replied, "No, not if they are pure."

Prof. Speyers said that the most interesting point to him was the solubility of the glutinoids in a mixture of alcohol and water, when it appeared that they were insoluble in either water or alcohol alone.

Dr. Osborne thinks there may be a hydrate formed by taking up water from the dilute alcohol, and this hydrate then dissolves.

Dr. Smith said that no one who had not worked in this difficult subject could appreciate the value of Dr. Osborne's work, and especially the classification which had been made of the compounds.

Mr. Hewitt suggested a method of separating the proteids by availing of the different behavior of solutions of different osmotic pressures, and described experiments in which he had used membranes prepared with gelatine treated with formaline, which he found more satisfactory than potassium bichromate or tannin for making the gelatine insoluble. He had also found that the results differed when bichromate or tannin were used.

Prof. Austen asked if the vegetable proteids are entirely dif-

ferent from the animal, and if there is any classification of the latter.

Dr. Osborne said that superficially they were quite similar, but closer study revealed marked differences. Nearly all authors of physiological chemistries give classifications for these proteids, but that most of these authority differ to a greater or less extent from one another. The most comprehensive classification of the animal proteids that he had seen was that given by Prof. Chittenden in his Cartwright lectures for 1894.

Mr. J. H. Wainwright read a paper on the "Determination of Solid Fats in Artificial Mixtures of Vegetable and Animal Fats." He said that the problem was to make analyses of mixtures of solid fats and vegetable oils, as cottonseed-oil, lard, and oleostearin which might be classed as compound lards, of which "cottolene" was an example; the chief object being to ascertain the percentage of oleostearin.

In simple mixture as cottonseed-oil and stearin, the analysis can be readily made by determining the constants of the fat, iodine number, etc. But in a compound lard containing lard itself, the determination of constants gives very little satisfaction, owing to the confusing effect of the lard. Experiments were made on special mixtures with the result of proving that under pressure at ordinary temperatures both cottonseed-oil and lard are removed, leaving the stearin.

At temperatures much above 75° F. or much below 70° F. the error was considerable, but within these limits he had obtained results differing not more than a half per cent. from the correct figure. Until the method was further perfected, he allowed a plus or minus error of one and a half per cent.

CINCINNATI SECTION.

The regular meeting of this section was held on Tuesday evening, December 17, 1895, Dr. Alfred Springer presiding.

Prof. T. H. Norton spoke of the loss sustained by the section in the death of Chauncey R. Stuntz, professor of physics and chemistry at Woodward High School, and moved that Messrs. F. Hornburg, E. Twitchell, S. P. Kramer, and H. B. Foote, all former students of the deceased, be appointed a committee to draft resolutions of respect. Prof. Stuntz was one of the bes

known educators in the Ohio Valley and one of the organizers of the chemical society of Cincinnati and vicinity, which afterward became the Cincinnati Section of the American Chemical Society. He was elected chairman for 1893, and his earnest work in behalf of the Section was highly appreciated by all the members.

Prof. J. U. Lloyd read a paper on "Percolation" and gave a practical demonstration of packing the percolator.

The committee appointed to nominate officers for the Section for 1896 reported the following ticket:

President, E. Twitchell.

Vice Presidents, Prof. O. W. Martin and Chas. G. Merrill.

Treasurer, H. B. Foote.

Secretary, E. C. Wallace.

Directors, Dr. S. P. Kramer, Dr. S. Waldbott, Dr. John McCrae.

On motion the secretary was instructed to cast the ballot of the Section in favor of the above ticket.

Issued with February Number, 1896.

Proceedings.

TWELFTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The twelfth general meeting of the American Chemical Society was held in Cleveland, Ohio, December 30th and 31st, 1895.

The first session was called to order by the president, Dr. E. F. Smith, at 9.15 A. M., Monday, December 30th, in the Chemical Lecture Room of the Western Reserve Medical College.

Mr. M. S. Greenough, President of the Cleveland Gas Light and Coke Company, was introduced and gave the following words of welcome:

Gentlemen of the American Chemical Society:

It is with great pleasure that I have accepted the invitation of Prof. Mabery to act as spokesman for the local interests to which you are allied, and welcome you to the hospitalities of our city. Cleveland is a very popular city for conventions, and I am informed that no less than 100 have met here during the year now closing. I venture, however, to assert that no body of men gathered together in this vicinity or elsewhere could represent a profession more useful or honorable than your own. What civilization owes to chemistry is hardly appreciated by the ordinary citizen. He is so accustomed to enjoy the health, comfort and prosperity which comes from it, that he looks upon his blessings as part of the natural order of things, and never stops to consider to what he is indebted for them. When man was in his primitive state and dressed in skins, lived in a tent on what he could kill and changed his residence daily, he naturally had not much use for chemistry, but nowadays without the expert analyst we should be simply helpless. We depend upon him to know that our drinking water is safe to use, whether our children's milk is genuine or diluted, whether our groceries are pure or adulterated. We invoke his assistance in every department of manufacture. In the steel business, for instance, which is the right hand of this city, the buyer purchases on a guaranteed percentage of ingredients, and every blow is tested, aud where iron ores are saleable or unsaleable according to their chemical composition, there the chemist is absolutely indispensable. It might be truly

said that without the constant, persistent, almost unnoticed work of the chemist, this city of Cleveland, with its diversified interests, including every sort of steel work, with its paint works, its refineries, its chemical works and its great ship yards, would be a small town, one-tenth its present size, with gardens and orchards coming down to the Public Square. Cleveland is built on the work of the expert chemist, and yet not one man in a hundred ever stops to realize that fact.

My own business is to furnish illuminating gas to this community and, of course, no man here knows so well as I how much that industry is indebted to chemistry. When I left Harvard College, twenty-seven years ago, and entered the service of the Boston Gas Co., gas sold at $2.50 per thousand ; now it is sold there at a dollar, and here this company only nets seventy-five cents for its product, after paying to the city our franchise tax of six and one-half per cent. This is not all due directly to chemistry, but a great part of it is. An old-fashioned gas manager is reported to have said "I don't care a d—n about your hydrogens and your oxygens ; you give the coal and I'll cook the gas out of it." Such a man was once very useful, and may be still, but if everybody had held his opinions gas would not now be sold so cheap or pure. There is not a large company in this country to-day but what either employs a permanent chemist or has one near by on whom to call. Before the chemist lent his aid gas companies either ran their tar and ammonia into the nearest river, or else burned their tar and left their ammonia in the gas. Without his experience and analyses we should never have applied the principles of regenerative gas firing to our retort benches or our gas burners. We should have failed in the successful enrichment of decomposed steam by petroleum products, which has been a development of the last twenty years, and which furnishes the method by which gas can be most cheaply made in many localities in this country.

Auer Von Welsbach was an Austrian chemist who discovered the luminous qualities of some rare earths, by heating which a foot of gas is enabled to give three times as much light as is ordinarily obtained by burning it, and by which gas has been furnished with its strongest weapon in the fight for business. Last of all is this new discovery of calcium carbide with its product of acetylene, which affords the most beautiful artificial light yet produced : and though I am by no means prepared to endorse the claims of its enthusiastic advocates, yet it must have its effect upon the lighting interests of the whole country of every description. "Every man to his last" says the shoemaker, and I speak of these things because they have come under my own

eyes; but I have no doubt that every manufacturer in this city might be heard from in a similar strain as to the cheapening and improving of his product by the skill of your profession. I know that I speak for them all when I welcome you to our city, and dwell upon the respect in which we hold you.

You will find upon the programs a large number of enterprises which you are invited to visit. The gas works are not upon the list, but if any of your body are interested in that direction you will find our works on Wilson Avenue a good example of modern gas engineering.

I sincerely trust that you will find your stay here both agreeable and interesting, and that we may have the pleasure of seeing you again, either individually or collectively.

If there are any eastern members of your body who are considering the advisability of moving westward, you will, I am sure, take home with you for reflection the great future which is awaiting this city and its environs, and will also realize the opportunities which are awaiting the man who settles among us thoroughly equipped with the education of the industrial chemist.

In response, Dr. E. F. Smith, President of the American Chemical Society, said:

Believe me, sir, that the American Chemical Society fully appreciates the cordial and hearty reception that has been extended to its members, and through me returns to you and those whom you represent, its sincere thanks.

We are glad to be here, and we are eager to avail ourselves of the many opportunities which we shall have while in your midst, of inspecting the many industrial plants within the borders of this city, and within its immediate neighborhood.

We feel particularly grateful to our Council for having called us here, where there is such a centralization of enterprises founded on scientific principles. I can assure you, we will take advantages of the privileges which you have offered to us.

We feel happy, too, in the thought that in coming here we have a chance to meet with your local chemists, who are a host within themselves. They have wrought well, and they have contributed very largely to placing the name of your city upon a high pedestal among the cities of this nation which encourage industries founded upon chemical principles and processes. Two of them particularly are we proud of: I need not mention the names of Dr. Morley and Dr. Mabery, the first of whom has won for himself a reputation by his investigations on certain constants of nature; and the second has achieved equal glory by

the researches which he has made, and the light which he has thrown upon the difficulties surrounding the petroleum problem.

For these reasons, and for the opportunities which we hope to have while here of inspecting these great industries, and for the kindly reception given us and the many hospitalities which will be ours while we are here, we thank you.

I trust that you, and all Cleveland for that matter, if convenient, will attend our session and join in the discussions of the papers which are to be presented. (Applause.)

The President then called for the report of the General Secretary, which was read, and by vote of the Society was ordered placed on the file. The Secretary's report is as follows:

To the Members of the American Chemical Society:

GENTLEMEN:—The record of the American Chemical Society during the past year has been one of enlarged activities, and of higher attainments and more extended usefulness than ever before. The membership of the Society has steadily increased; three new local sections have been established and many of the older sections have made commendable progress in numbers and in the character and influence of their work; the journal has been much improved, and the Society to-day exerts a more potent influence among chemists, both in the old world and the new, than it did one year ago.

The roll of membership December 26, 1894, was as follows:—Members, 720; associates, 55; honorary members, 8: total, 783. On December 26, 1895, there were 884 members, 58 associates, and 8 honorary members; total 950. If to this number we add the names of 54 persons, who have been elected, but have not yet qualified, (a great majority of them having been elected since the 1st of November, and according to the constitution, not being required to qualify before January 1st), and 31 whose applications for membership are now under consideration, we have a grand total of 1035, which may be considered the present numerical strength of the Society. The increase in membership during 1895 has been greater than in any previous year, except 1894, and there is reason to believe that the momentum which the Society has acquired in this direction during the past few years will continue for a long time to come.

The following named members have died since the presentation of the last annual report of the General Secretary: A. A. Fesquet, H. B. Nason, J. C. Dittrich, W. H. Whalen, Mark Powers, Lewis W. Hoffman, G. E. Moore, W. G. Wallace and Wm. C. Wilson. This list was reported to the Society at the Springfield meeting last August, and sketches of Prof. Nason, one of the ex-Presidents of the Society, and of Dr. Moore, one of the most highly respected members of the New York Section, have appeared in the Journal of the Society.

The three local sections established during the past year are located respectively in Chicago, Nebraska and North Carolina.

There are now nine local sections of the Society, viz;

Rhode Island Section: Presiding Officer, Charles A. Catlin, 133 Hope St., Providence, R. I.; Secretary, Walter M. Saunders, Olneyville, R. I.

Cincinnati Section: Presiding Officer, Karl Langenbeck, 27 Orchard St., Zanesville, Ohio; Secretary, E. C. Wallace, Room 71, Blymeyer Building, Cincinnati, Ohio.

New York Section: Presiding Officer, Peter T. Austen, Polytechnic Institute, Brooklyn, New York; Secretary, Durand Woodman, 127 Pearl St., New York City.

Washington Section: Presiding Officer, Charles E. Munroe, Columbian University, Washington, D. C.; Secretary, A. C. Peale, 605 12th St., N. W., Washington, D. C.

Lehigh Valley Section: Presiding Officer, Edward Hart, Lafayette College, Easton, Pa.; Secretary, Albert H. Welles, Lafayette College, Easton, Pa.

New Orleans Section: Presiding Officer, A. L. Metz, Tulane Medical College, New Orleans, La.; Secretary, Hubert Edson, Bartels, La.

Chicago Section: Presiding Officer, Frank Julian, South Chicago, Ill.; Secretary, F. B. Dains, 2421 Dearborn St., Chicago, Ill.

Nebraska Section: Presiding Officer, H. H. Nicholson, University of Nebraska, Lincoln, Nebraska; Secretary, John White, Box 675, Lincoln, Nebraska.

North Carolina Section: Officers not yet reported.

The financial outlook of the Society is very encouraging; the report of the Treasurer shows a good balance after paying all

indebtedness. A little well directed effort on the part of the members to secure advertisements for the Journal, and increase the regular and associate membership, would add very materially to the income of the Society and would enable the Committee on Papers and Publications to enlarge the scope of the Journal, and to make it in many ways even superior to what it is at present.

The membership dues have been collected by the General Secretary during 1895 as in the previous years. This work has been looked after very closely, and the results have been of twofold advantage to the Society—a considerable sum has been secured that otherwise would have been lost in unpaid arrears, and those who have paid their dues, after repeated reminders from the Secretary, have been saved to the membership of the Society, and have been more prompt the next time in their remittances.

During the year 1895 it has been necessary to drop the names of only twelve persons from the roll of the Society, as required by the constitution, for non-payment of arrears.

During the year Prof. F. W. Clarke resigned as Chairman of the Committee, appointed by the Council, for considering the question of revising the constitution, and Dr. H. W. Wiley was appointed to fill the vacant position. This committee has not yet completed its work. Under the authority and direction of the Society, the General Secretary secured the passage of a bill by the New York Legislature, enabling the Society to choose its directors without regard to their being residents of the State ot New York, or any other State or locality, and also legalizing whatever action the Society might take at any of its meetings held outside of New York State.

Prof. Clarke presents his annual report on atomic weights as a paper to be read at this meeting. The Society is to be congratulated in having among its members a person so able and at the same time so willing to present fully a regular annual report upon this subject.

During the year the President, upon the authority of the Council, appointed Messrs. Hale, Austen and Breneman as a committee to consider the question of a permanent badge for the

Society. The committee have met and considered the subject and requests for suggestions and designs have been sent to every member of the Society, but no report has yet been prepared.

The Society held its eleventh general meeting in Springfield, Mass., August 27th and 28, 1895, just previous to the meeting of the American Association for the Advancement of Science in the same city. There was a large attendance and a full program of papers. The meeting was one of unusual interest and inspiration to all who were fortunate enough to attend. A full account of the proceedings was published in the October number of the Journal.

Early in the year formal invitations were received from the officials of the city of Cleveland, the Chamber of Commerce of Cleveland, the Western Reserve University, the Case School of Applied Science and the Cleveland Chemical Society, for the American Chemical Society to hold their annual meeting this year in Cleveland. These invitations were so hearty, and Cleveland is so desirable a city in which to hold a meeting of the Society, that the Council gladly accepted the invitations, with the result that we are now the favored guests of these bodies and enjoying their cordial and unstinted hospitalities.

It is much to be regretted that every member of the Society could not be present to partake of the rich feast we find prepared for us in this beautiful and enterprising industrial and educational center.

In looking back upon the past, carefully surveying the present condition and attainments, and anticipating the future, the members of the American Chemical Society have every reason for encouragement and gratification.

If the Society could receive from all its members the loyalty and active support which has always been given by those who have been most devoted to its interests, the rapid progress of the past few years would be regarded as little when compared with what the next decade would witness. May we not hope as we begin this new year in our history that this active support and loyality will be accorded, and that every member will to the utmost of his ability exert himself to increase the membership,

the strength and the influence of the Society, both at home and abroad.

We sometimes feel that we need to establish a league of loyal Americans in the realm of chemical science; whatever Americans accomplish should go to the credit of America. But this is not all; we believe it is a mistake for any chemist under the existing conditions to think that his best path to recognition by the scientific world lies through the medium of foreign periodicals. Articles published in our Journal are so fully abstracted and so often copied entire by foreign scientific periodicals that it seems that the best means for securing general publication and widespread recognition for any deserving paper is through the columns of our Journal. Thus not only loyalty to the American Chemical Society, but also self interest demands that the columns of our Journal be kept filled with the records of the best work done in our country.

Respectfully submitted,

ALBERT C. HALE.

BROOKLYN, N. Y., Dec. 26, 1895. *General Secretary.*

FINANCIAL REPORT, 1895.

Received for dues from Dec. 1, 1894 to Dec. 14, 1895	$4,365.75
Retained as Commission	436.50
Balance for the A. C. S. Treasurer	3,929.25
Paid A. C. S. Treasurer (as per vouchers)	3,825.00
Balance not yet forwarded	104.25
Interest	11.48
Balance on Deposit	115.73

ALBERT C. HALE,

Dec. 14, 1895. Gen. Sec. A. C. S.

In the absence of the Treasurer his report was read by the General Secretary, as follows:

NEW YORK, December 26, 1895.

TREASURER'S REPORT FOR THE YEAR 1895.

Receipts.

Balance on hand Dec. 21st, 1894	$ 505.95
Net dues and interest received from the Gen'l Secretary	3,940.73
Cash received for subscriptions to Journal	624.93
" " " back numbers	122.82
" " " advertisements in Journal	517.74
Interest from Farmers' Loan and Trust Co	9.80
	$5,721.97

Disbursements.

For expenses of Treasurer's office		$	11.35
" " " Gen'l Sec'y office			494.03
" " " Editor's office			56.40
" " " Librarian's office			78.18
" " " Springfield meeting			42.17
" general expenses			67.30
" salary of editor			250.00
" publication of Journal			3,244.15
" insurance			30.00
" rebates to Local Sections, as follows:			
New York Local Section	$ 195.98		
Washington " "	103.33		
Lehigh Valley "	30.00		
Cincinnati " "	60 00		
Chicago " "	38.33		
Nebraska " "	21.67		
			449.13
Balance on hand Dec. 26th, 1895:			
In Farmers Loan and Trust Co	$ 443.63		
In Bank of Metropolis	356.90		
Checks on hand	184.15		
Cash on hand	12.00		
Postage stamps	2.40		
			999.08
			$5,721.97

The following report of the Librarian was read by the General Secretary:

DECEMBER 26, 1895.

The library has been in storage during the year and therefore there is little to report. It is hoped, however, that a suitable place where the books may be useful to the members will soon be found. Several places have been suggested but none as yet that meets the requirements of the case.

There is a growing call for back numbers of the Journal and I would suggest that the money obtained from their sale be used to find and care for the library.

The Librarian has received the following exchanges:

UNITED STATES.

American Chemical Journal.
American Journal of Pharmacy.
American Manufacturer and Iron World.
American Naturalist.
Annals of the New York Academy of Arts and Sciences.
Anthony's Photographic Bulletin.

Bulletin of the American Museum of Natural History.
Deutsch-Amerikanische Apotheker-Zeitung.
Engineering and Mining Journal.
Ephemeris (Squibb).
Engineering Magazine.
Journal of the Franklin Institute.
Journal of the United States Artillery.
New York Medical Journal.
Oil, Paint, and Drug Reporter.
Popular Science Monthly.
Proceedings of the Academy of Natural Sciences (Philadelphia).
Proceedings of the American Academy of Arts and Sciences (Boston).
Proceedings of the American Philosophical Society (Philadelphia).
School of Mines Quarterly.
Scientific American.
Technology Quarterly.
Textile Colorist.
Textile Manufacturers' Review and Industrial Record.
Transactions of the American Institute of Electrical Engineers.
Transactions of the American Institute of Mining Engineers.
Transactions of the New York Academy of Sciences.

CANADA.

Journal and Proceedings of the Hamilton Association.
Proceedings of the Canadian Institute.
Proceedings and Transactions of the Nova Scotia Institute of Sciences.

HOLLAND.

Revue Internationale des Falsifications.

ITALY.

Gazzetta Chimica Italiana.

ENGLAND.

Analyst.
Chemical News.
Engineering.
Journal of the Chemical Society.
Journal of the Society of Arts.
Journal of the Society of Chemical Industry.
Oil and Colorman's Journal.
Pharmaceutical Journal and Transactions.
Sugar Cane.
Transactions of the Institute of Brewing.

FRANCE.

Annales des Mines.
Bulletin de la Société Chimique de Paris.
Bulletin de la Société Industrielle de Rouen.
Bulletin de la Société Industrielle de Amiens.
Moniteur de la Teniture.
Moniteur Scientifique de Quesnesville.
Reportoire de Pharmacie.

GERMANY.

Archiv der Pharmacie.
Bierbrauer.
Bulletin de la Société Industrielle de Mulhouse.
Sitzungsberichte der K. B. Akademie der Wissenchaften zu München.

AUSTRIA.

Allgemeine Oesterreichische Chemiker und Techniker Zeitung.
Oesterreiches Zeitschift für Berg und Hüttenwesen.
(Proceedings) Kaiserliche Akademie der Wissenschaften in Wien.

RUSSIA.

Bulletin de l'Academie Imperiale des Sciences de St. Petersburg.
Memoirs de la Société des Naturalistes de Kiew.

AUSTRALIA.

Journal and Proceedings of the Royal Society of New South Wales.

ROUMANIA.

Buletinul Societatii de Sciinte Fizice.

The Librarian wishes to acknowledge the receipt of the following volumes:

Chemical Bulletins U. S. Department of Agriculture.
Reports and Bulletins of the Massachusetts Experiment Station.
Reports and Bulletins of the Connecticut Agricultural Experiment Station.
One hundred years of business life, Wm. J. Schieffelin.
An Introduction to the Study of Rocks. Presented by the Trustees of the British Museum of Natural History.

Respectfully submitted,

F. E. DODGE,
Librarian.

Dr. Hart was then called upon and made a report for the Committee on Papers and Publications.

He stated that last year 915 pages of the Journal were published, this year we published 1092 pages, and we have enough papers left over to fill the January number and part of the February number. The committee have been hampered in their plans by the financial condition of the society. But the treasurer's report is an encouraging one, and we hope next year, if we are to go on with the work, to show still better results.

I may say that there are frequent complaints of non-delivery of the Journal from members of the society. The difficulty in most cases is not in sending out, but with the post-office authorities, who are so overwhelmed with second-class matter that they become careless. The Journal is mailed as carefully as it is possible to do it, the address printed and kept standing, and there are very few mistakes made in the office of distribution. I hope that members who do not receive the Journal regularly will write to us, and we will make every effort to get the Journal to them. Very often when a complaint has been made of non-receipt of the Journal, another Journal has been sent, and the second one has not been received. The difficulty seems to be with Uncle Sam's method of conducting business.

Several plans have been suggested and considered for increasing the efficiency of the Journal, but nothing that has been suggested is yet ready for report.

The question of a good journal is largely a financial question. If we have money to print and circulate a journal, we can have a good journal. There is no difficulty about papers. We have more good papers now than we can manage.

It would perhaps be interesting to the members to know something about the actual circulation of the Journal, which is considerably in excess of the membership. We sent out for December 1125 Journals. Of this number less than fifty are exchanges, so our actual paid subscription list is very nearly 1100. The returns for the next year are beginning to come in, and I am able to report large accessions to the number of subscribers, especially foreign subscribers.

Prof. Sabin reported for the Finance Committee.

Formal reports were then made by members of special committees as follows:

Committee on Duty-Free Importation, C. E. Munroe; Committee on Nomenclature and Spelling of the Journal, Edward Hart; Committee on Triennial Congress of Chemists, F. W. Clarke.

The Secretary then read a letter from Dr. T. H. Norton, of Cincinnati, expressing his regret that he was unable to attend the meeting and sending his best wishes for an enjoyable and profitable occasion.

The following communication was then read by the Secretary:

DEPARTMENT OF THE INTERIOR,
UNITED STATES GEOLOGICAL SURVEY.
WASHINGTON, D. C., November 30, 1895.

To the President of the American Chemical Society:

SIR: In compliance with a request emanating from the Chemical Division of this survey, I address you as the head of the most representative body of the American chemists with a view to securing action on the part of the American Chemical Society looking toward the general adoption, in this country at least, of a method for the proximate analysis of coal.

The prevailing method of proximate analysis, though unscientific and far from satisfactory, is still capable of affording information which is valuable, as chemists and geologists know, both as a preliminary to more extended scientific examination and as to the value of coal for one or the other of the uses to which it may be put as a fuel. But in practice such wide diversity exists in the details of this method that the analysis of different series of coals, made by different chemists, are seldom of much value for purposes of comparison, since concordant results are only to be attained by a rigid adherence to a certain order of procedure.

This matter is of great importance to geologists and chemists as well as to those who contemplate investing in coal properties and to many large consumers of coal. A uniform method of analysis, which should also cover the determination of sulphur in coals seems therefore very desirable, and the adoption of such a method can most readily be brought about by the authoritative sanction of the American Chemical Society.

I would make the suggestion that a committee of chemists experienced in coal analysis be appointed with instruction to

gather from all sides the views of those whose opinions are likely to be of value in connection with their own, and from the data thus collected to formulate in minute detail a method which may come to be accepted as the one by which all analysis of coal and coke in this country shall be made.

It is not necessary that a novel method be devised, but only that the diversity in detail now practiced be reduced to uniformity by the selection of those features which in the judgment of the committee will most nearly meet the exigencies of the case.

Yours with respect,

CHAS. D. WALCOTT.
Director.

On motion of Prof. Edward Hart it was resolved that the President appoint a committee of three to take into consideration Prof. Walcott's communication and present a report upon the same at the Summer meeting.

After some announcements by the General and Local Secretaries, A. A. Bennett read a paper on "The Quantitative Determination of the Halogens in the Presence of Each Other;" and Wm. McPherson presented a paper on "Constitution of Oxyazobenzene." The latter was discussed by Drs. Prescott, Hart and Mabery.

In the absence of the author a paper by Willis E. Everette on the "Method of Analysis of Nickel and Cobalt in Ores," was read by the General Secretary, and was afterwards discussed by Drs. Mabery and C. B. Dudley.

A. B. Prescott then presented a paper prepared by himself and S. H. Baer on the "Melting Points of Certain Homologous Pyridine Derivatives," and this was followed by another paper entitled "Pyridine Alkyl Hydroxides," by the same authors. These papers were discussed by Drs. Fireman, Smith and Hart. After some announcements the session adjourned.

In the afternoon visits were made to various works in Cleveland, and in the evening the laboratories and lecture rooms of Adelbert College and the Case School of Applied Science were inspected, after which the Society held an evening session.

The evening session of the Society was called to order by President Smith, at 8.15 P. M. in the Chemical Lecture Room of the Case School of Applied Science. After some announcements by the General Secretary, Dr. Chas. F. Mabery was introduced

and delivered a very valuable and interesting address upon petroleum. Prof. Mabery gave an account of the experimental methods, products, and results connected with work now in progress on American petroleums. The different forms of stills employed in fractional distillation both under atmospheric pressure and in vacuum were shown, together with the apparatus for distillation under diminished pressure when many operations are in progress. The determination of sulphur in gases, liquids, and solids was described and illustrated by the apparatus.

Representative crude oils from the Oil Springs and Petrolia fields in Canada, from the Lima and Findlay fields in Ohio, and the Berea grit sandstone in Ohio were exhibited and their composition given as well as the composition of representative oil rocks,—the Corniferous limestone, the Trenton limestone, and the Berea Grit sandstone.

A distillation now in operation for the separation of the butanes and pentanes from a very light gasoline (92°) in which a distillate was collecting below —10° was shown in operation, together with other distillates with low boiling points, and their halogen derivatives which are now under examination for the purpose of establishing the identity of the butanes. The purified octanes and some of their halogen derivatives were also described.

Prof. Mabery read a letter from Professor Markownikow of Moscow, which stated that Professor Markownikow had given no attention to Pennsylvania petroleum. In one of his papers, the suggestion had been made that the Pennsylvania oil might prove to contain the naphtenes. This assertion from Professor Markownikow was obtained to correct the erroneous statements in German and American works on petroleum that Markownikow had examined Pennsylvania petroleum.

Professor Mabery exhibited many specimens of hydrocarbons which had been separated from Berea Grit, Ohio, Canada, and Pennsylvania petroleums for the purpose of ascertaining the composition of these oils above 150°.

A number of specimens of sulphur compounds, including sulphides and unsaturated hydrocarbons were shown that had been separated from Canadian petroleum.

After the address several questions were asked of Dr. Mabery and various points were discussed by Drs. Dudley and Prescott; Profs. Moulton and Breneman and Mr. Frasch. Upon motion of Dr. Hale, the Society passed a unanimous vote of thanks to Dr. Mabery. The evening session then adjourned.

The morning session of Tuesday, December 31st, was called to order by President Smith at 9.10 A. M. After some announcements by the General Secretary, the President named the members of the Committee on Coal Analysis, in accordance with the request received by communication from Prof. Walcott. The committee named were: Drs. W. F. Hillebrand, C. B. Dudley, and W. A. Noyes.

Mr. James Otis Handy then read a paper on "Improved Methods for the Analysis of Aluminum, Alumina and Bauxite;" this was followed by a paper on "The Cyanide Method of Extracting Gold from its Ores," by Wm. J. Martin, Jr., read by the General Secretary in the absence of the author.

A paper on "The Use of the Calorimeter in Detecting Adulterations of Butter and Lard," by E. A. de Schweinitz and James A. Emery, was read by Prof. Sabin, the authors of the paper being absent. Prof. Sabin also discussed some of the points contained in this paper.

A paper by H. W. Wiley on "Determination of the Heat of Bromination in Oils," was read by. Dr. C B. Dudley, Dr. Wiley being absent. This paper was discussed by Dr. Dudley and Prof. McPherson.

After some announcements by Dr. Mabery regarding the afternoon excursion, a paper on "Technical Analysis of Asphaltum" by Miss Laura A. Lynton was read by Dr. Prescott, and was discussed by Prof. Sabin, Drs. Mabery and Prescott.

A paper on "The Microscopic Detection of Beef Fat in Lard" by T. S. Gladding, was read by Dr. Hart, after which Prof. F. W. Clarke's Annual Report on the Atomic Weights of the Elements was read by Prof. Breneman and discussed by Drs. E. F. Smith, Edward Hart, and C. B. Dudley.

The report of the canvassers for the election of officers for the year 1896 was presented by the Secretary and the following

named persons were declared elected: President, Chas. B. Dudley; General Secretary, Albert C. Hale; Treasurer, Chas. F. McKenna; Librarian, Frank E. Dodge. Directors to serve two years: Chas. F. Chandler, Peter T. Austen, Chas. E. Munroe, Albert B. Prescott. Councilors to serve three years: J. W. Mallet, Albert B. Prescott, T. H. Norton, G. C. Caldwell.

The retiring President, E. F. Smith, then introduced the President-elect, Chas. B. Dudley, with a few congratulatory words to the Society in having secured a man so worthy to occupy the position. After a brief and appropriate response by Dr. Dudley, he was requested to occupy the chair while the retiring President presented his address on "A Glance at the Field of Electro-Chemistry."

On motion of Prof. Sabin, the Society passed a vote of thanks to the Mayor and the Cleveland Chamber of Commerce, the Western Reserve University, Case School of Applied Science and the Cleveland Chemical Society for their kind invitation to hold the Twelfth General Meeting of the American Chemical Society in Cleveland, and for the courtesies extended to the Society during their meeting. The thanks of the Society were also voted to the members of the Local Committee on Arrangements, to the proprietors and managers of the various works visited, to those who received the chemists and conducted them through the works, and to the persons who conducted the various excursions and visits.

Upon motion of Dr. Dudley, a vote of thanks was given to the retiring President, the General Secretary and the Editor for the highly satisfactory manner in which they had discharged the duties of their respective offices and to those who had prepared papers for the meeting.

Dr. Mabery, President of the Cleveland Chemical Society, expressed the great pleasure felt by the people of Cleveland at the honor the Society had conferred upon them in visiting their city, and also the appreciation which they felt of the advantages this visit had conferred upon them.

Dr. A. B. Prescott, one of the ex-Presidents of the Society, was called upon by President Smith for some remarks, and spoke briefly of the rapid growth of the Society, not only in

numbers but also in general tone and character of its work. The Twelfth General Meeting of the American Chemical Society was then adjorned.

ALBERT C. HALE,
General Secretary.

EXCURSION TO THE WORKS OF THE GRASSELLI CHEM. CO.[1]

This was the only excursion scheduled for Tuesday afternoon, December 31. It was joined by nearly every visiting and local chemist and was in charge of Mr. Edwin F. Cone, experimental and research chemist of the company. Chemists to the number of seventy-five assembled at a convenient locality and were transported by electric cars to the plant of the company located in the southern part of the city. Here they were met by Messrs. E. R. Grasselli, T. S. Grasselli, J. P. Lihme, gentlemen of the operating department, and others, and were escorted through the plant. This company operates ten different large chemical plants in various parts of the country, one of the largest being the works visited in Cleveland.

The following were the points of interest that were inspected:

Sulphuric Acid.—Several systems are operated here for burning lump and fine ore, the latter being especially adapted for such work. Only pyrites is burned obtained from different parts of this country and abroad. The construction of these plants was found to be modern and the equipment equal to the best.

In connection with these systems are the concentrating plants where sulphuric acid in large quantities is concentrated to its various commercial strengths.

Nitric Acid.—In this plant nitric acid was seen in process of manufacture from Chile saltpeter on a large scale. In connection with this was a plant for the production of different grades of acid for the trade.

Hydrochloric Acid.—This plant comprises various modern devices for the manufacture of numerous qualities of muriatic acid. Sodium chloride and nitre-cake are used to a large extent. Salt-cake from these plants is worked up in large quantities and sold to glass manufacturers.

[1] This description, written by E. F. Cone, was received too late for insertion in the report of the General Secretary.

Mixed Acids.—In this department sulphuric and nitric acids of proper strengths are mixed in such proportions as the trade demands and sold in large quantities to dynamite manufacturers.

Glycerol.—This plant is adapted to the manufacture of chemically pure glycerol, which is obtained on the large scale from crude glycerol by distillation with steam. This department has achieved considerable reputation for the quality of the product, which is equal in every respect to any in the market. Great care is exercised in its manufacture and many chemical tests made to insure a high-grade article. A beautiful product is made and each visitor was presented with a small bottle as a souvenir.

Ammonia.—In this extensive plant large quantities of ammoniacal liquor are worked up into all grades of aqua ammonia, ammonium sulphate and other ammonia products.

Laboratories.—The different laboratories were visited and chemists were found busy in many operations of interest to the analytical and research chemist.

The extensive shops of the company as well as the sal-soda and Glauber's salt plants were also visited.

A pleasant and agreeble surprise awaited the party after the tour of inspection. In the work's office of the company a spread was served, in every way adapted to appease the hunger and quench the thirst caused by the long tour of the afternoon. After the cigars had been passed and a social chat indulged in, the party were transported back to the city by cars. The excursion was voted by one and all a most delightful and instructive one.

BOARD OF DIRECTORS.

Resolved, That the Editor be and he is hereby instructed to mail regularly to the Secretary of each Local Section of the American Chemical Society a copy of the Journal for the use of the section, upon written request of the Chairman and Secretary of the Section.

NEW MEMBERS ELECTED DECEMBER 26, 1895.

Bartlett, Edwin J., Dartmouth College, Hanover, N. H.
Bomberger, F. B., College Park, Md.

Boot, Johannes Cornelius, 24 East 20th St., N. Y. City.
Gray, Marietta, care of University of Nebraska, Lincoln, Neb.
Hilliard, H. J., 204 Columbia Heights, Brooklyn, N. Y.
Hollinger, Myroen John, Sharpsville, Mercer Co., Pa.
Hunicke, H. Aug., 1219 Mississippi Ave., St. Louis, Mo.
Skinner, W. W., College Park, Md.
Summers, Bertrand S., Western Electric Co., Chicago, Ill.
Wigfall, Edward Newton, 1822 Arch St., Phila., Pa.,

ASSOCIATES ELECTED DECEMBER 26, 1895.

Allison, William O., William St., N. Y. City.
White, Richard A., Grand Central Station, N. Y. City.

NEW MEMBERS ELECTED JANUARY 18, 1896.

Bartow, Edward, Williamstown, Mass.
Battle, H. B., Ph.D., Raleigh, N. C.
Foulk, Chas. W., B. A., Ohio State Univ., Columbus, Ohio.
Fox, H., 1224 Rookery Building, Chicago, Ill.
Graves, George H., 358 State St., Bridgeport, Conn.
Hall, Clarence, Aetna, Lake Co., Indiana.
Hartwell, Burt L., B.Sc., Kingston, R. I.
Hicks, Edwin F., 52 Beaver St., N. Y. City.
Hopkins, Cyril George, 204 So. 4th St., Champaign, Ill.
Magrunder, E. W., Johns Hopkins Univ., Baltimore, Md.
McGeorge, Arthur, 205 West 78th St., N. Y. City.
Pickering, Oscar W., 2 Milk St., Newburyport, Mass.
Pitman, John R., Frankford Arsenal, Phila., Pa.
Rhodes, Edward, Highfields, Fordsham, Cheshire, Eng.
Sargent, Chas. S., B.Sc., Peace Dale, R. I.
Seal, Alfred Newlin, 1418 Bouvier St., Phila., Pa.
Warwick, Arthur William, Wickes, Mont.
Williams, Charles B., B.S., Raleigh, N. C.
Woodcock, Reginald C., 636 West 55th St.. N. Y. City.
Tennille, Geo. F., Ph.D., 519 West 33rd St., N. Y. City.

ASSOCIATES ELECTED JANUARY 18, 1896.

Brenke, Wm. Chas., 506 South 5th St., Champaign, Ill.
Gazzolo, Frank Henry, 930 West Green St., Urbana, Ohio.
Keeler, Harry, 506 South 5th St., Champaign, Ill.

CHANGES OF ADDRESS.

Grosvenor, W. M., Jr., New J. H. Wolfe Hotel, Cripple Creek, Colo.
Guild, F. N., College of Mont., Deer Lodge, Mont.

Johns, John, care of The Guppinheimer Smelting Co., Perth Amboy, N. J.

Jones, L. J. W., 2126 High St., Denver, Colo.

Maury, Geo. P., Braddock, Pa.

Munsell, C. E., 100 Horatio St., N. Y. City.

Parmly, Dalton, 9123 Ontario Ave., Chicago, Ill.

Prochazka, G. A., 138 W. 13th St., N. Y. City.

Rosell, C. A. O., 841 Broadway, N. Y. City.

Townsend, Clinton, U. S. Patent Office, Washington, D. C.

Voorhees, S. S., 2101 G St., N. W., Washington, D. C.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

A meeting was held November 14th, 1895. President Munroe in the chair, with thirty-five members present.

Messrs. H. B. Hodges and Allan Wade Dow were elected as members, and Messrs. W. W. Skinner and F. B. Bomberger as local associates.

Dr. Marcus Benjamin read a paper on "The Smithsonian Institution's Contributions to Chemistry from 1846 to 1896." He recalled the fact that Smithson was regarded as one of the most expert chemists in elegant analysis and thought this fact had much to do with the provision made for a chemical laboratory in the original program of the Smithsonian Institution. He then traced the history of the laboratory of the institution, mentioning the many chemists who have occupied it and whose work has been published by the institution. Among these were J. Lawrence Smith, Dr. Robert Hare, Edward W. Morley, Genth, Gibbs, Booth, Carrington Bolton, Clarke, Traphagen, Magee, and Tuckerman. The paper was concluded with a bibliography of the chemical papers published by the Smithsonian Institution.

Mr. Cabell Whitehead presented "Some Notes of a Recent Visit to European Mints." In the discussion of this paper reference was made to the explosions so common in the lighting of a Buffalo Dental Company's muffle furnace. Mr. Dewey said that these explosions can be avoided by raising the whole body of the furnace by a simple arrangement of movable levers and then slipping a lighted paper over the burner.

Under the title "Calcium Phosphide," Prof. Chas. E. Munroe described the process of manufacture which he invented and carried into operation at the U. S. Naval Torpedo Station in 1891. Iron crucibles were employed in which quicklime was heated to redness, when white phosphorus in sticks was added through an iron tube which passed through the cover. The process was so simple that it was eventually carried on by unskilled laborers. The phosphide was produced at a cost of twenty cents per pound, while in the market it was selling for $2.25 per pound. It was manufactured for use in automobile torpedoes while at practice, and was found so efficient that when a pound in its container was submerged in eighteen feet of water it gave a flame on the surface two feet in height, which continued to burn intermittently for three hours.

Discussion was by Messrs. Whitehead, Stokes, Kelly and Fireman.

NEW YORK SECTION.

The regular monthly meeting of the New York Section was held at the College of the City of New York, 23d street and Lexington avenue, on Friday evening, January 10th. The usual informal dinner preceded the meeting.

The meeting was called to order at 8 : 30. Prof P. T. Austin in the chair ; about seventy members present. After the reading of the minutes, Mr. Eimer was asked to describe some improved and novel apparatus which had been placed on exhibition by Messrs. Eimer & Amend.

Mr. G. C. Hemming, M.E., delegate for the American Society of Mechanical Engineers to the International Conference at Zurich, 1895, reviewed the "Present Status of Iron and Steel Analysis," calling attention to the discrepancies in some recent work of different chemists in determining the constituents of the same quality of steel, with special reference to carbon and phosphorus, and to the omission of the direct determination of iron, which he thinks conducive to overlooking such elements as titanium, tungsten and others, which are more often present than the usual iron analysis would indicate, as they are but infrequently determined directly.

He reviewed papers by German, French and English authors,

giving results of microscopic examination of iron, and methods of preparing the samples for examination, and described the group of carbon "compounds" recognizable under the microscope by suitable methods of surface etching.

He considers that the microscope has opened a field which marks a great advance in methods of determining the condition and quality of iron and steel, and thinks that chemical methods need great improvement to distinguish the conditions in which the carbon exists.

Mr. Rossi in discussing Mr. Henning's paper thought it would be very difficult, if not impossible, to recognize the different combinations of iron and carbon by chemical means, at least in the present state of chemical science, since there is so little outside of physical characteristics to distinguish them.

Prof. Breneman asked whether in a "burned" iron the microscope would show an amount of magnetic oxide proportionate to the degree of deterioration of the iron. Mr. Henning replied that this was practically so; that the oxidation progressed from the surface inward, and a properly polished and etched specimen piece would show, when examined by powers over 800 diameters, the grains of oxide interlaced with the iron, in a form readily distinguishable from the iron.

Dr. McKenna, while admitting the need for chemical methods of determining the number and kind of compounds, is of the opinion that physical methods must be employed in conjunction with chemical methods, and that while chemical methods may advance greatly, the physical methods ought never to be omitted or displaced. Prof. Breneman suggested that the manufacturers would contribute greatly to the advancement of the matter by having the expensive chemical investigations required conducted in their own laboratories at the iron works, where the practical side is already highly developed and the material for research abundantly supplied; and where the results are most wanted and can be instantly applied. He also brought out the looseness of the term "compound" as used by the physicist, and urged the importance of keeping a clear distinction between the true chemical compound and the mixtures which were inaccurately termed compounds. In reply to these remarks, Mr.

Henning said that several steel and iron companies in this country have already established very complete micrographic laboratories, where in three hours an accurate determination of the condition of any specimen of the daily output may be secured.

Mr. George C. Stone read a "Note on the Probable Production of Permanganate by Direct Combustion of Manganese."

In discussing this note, Dr. Rosell called attention to the fact that potassium permanganate, when heated to a red heat, will decompose, and that the other permanganates behave in the same way. In fact, the permanganates can only be made in the wet way. On the other hand, manganates are generally produced in the dry way, and they will stand a very high temperature.

If, therefore, a substance after having been heated to the temperature of the blast furnace, would dissolve in pure water with the well-known rich purple color of a permanganate solution, it seems almost certain that such a substance could not be a permanganate, but it could be a solution of a ferrate.

It is, of course, also possible that the water used for dissolving the substance in question was not pure, but accidentally contained some acid, whereby on dissolving, the manganate was converted into permanganate.

A second paper by Mr. Stone was entitled "Remarks on Mr. Auchy's Paper on the Volumetric Determination of Manganese." He reviewed the Volhard method and described the conditions under which he obtained the most satisfactory results. He found, that provided all the iron was oxidized, it made no difference whether nitric, sulphuric, or hydrochloric acid were used. The only difficulty occurred when the amount of manganese was extremely small, in which case it was extremely difficult to get the precipitate to cohere and give a clear solution in which to perceive the end reaction.

Dr. E. R. Squibb presented a paper on the "Manufacture of Acetone and Acetone-Chloroform from Acetic Acid," in which he reviewed the history of acetone from its first mention to the present date. Pelouze was quoted as mentioning acetic acid as the best source of acetone, its vapor being passed through a red-hot tube filled with pumice stone. It was shown that this sub-

stance was well known prior to 1848 and had been made in large quantity prior to 1882.

Dr. Squibb described his method of preparing acetone by destructive distillation of acetic acid, with water vapor in a rotary still.

In regard to acetone-chloroform he quotes Liebig as giving the preference to acetone as the most suitable compound for the preparation of chloroform.

The work of Böttger and Siemerling was described and the results obtained by them were reviewed. One-third of the acetone used was the largest yield of chloroform obtained by Böttger; its specific gravity was 1.31 and it always contained acetone.

The misleading results of Siemerling's work were accepted so implicitly and quoted so definitely in standard works of reference that the further progress of the manufacture of chloroform from acetone was for many years obstructed, and patents have been issued in which the claims were based on supposed improvements on these erroneous results.

The last paper of the evening, "Some Notes on Highly Compressed Gases," was read by Mr. J. S. Stillwell. He described some investigations which had been made of certain explosions of the containing cylinders.

Some investigators had claimed that the passage through a minute orifice of light under high pressure, 2,500 pounds to the square inch, would create sufficient friction and consequent heating to cause explosive union with any oils or fat which might be present, and which might be volatilized by the mentioned source of heat. The author had, in the course of practical experience, tested this point over a hundred thousand times, and was satisfied that the heat never rose to the danger point under normal conditions of working, and that a heat approaching 400° F. was necessary before danger of explosion need be feared. This high temperature of the compressed gas was never reached, except through some careless or accidental want of properly cooling the compressor cylinder.

The meeting adjourned at 11 : 15.

LEHIGH VALLEY SECTION.

The Annual Meeting of the Section was held in the laborator of Lafayette College, Thursday, Jan. 16, at 3 P. M. The ballot for the election were opened and counted according to the cor stitution, and the following were found to be elected for the er suing year:

Presiding Officer: Albert Ladd Colby.

Secretary and Treasurer; Albert H. Welles.

Member of Executive Committee; Edward Hart.

A letter from the General Secretary of the Society of Chemi cal Industry was read, thanking the Section for their kindnes to Thomas Tyrer and Ludwig Mond.

The Secretary was instructed to furnish abstracts of the pro ceedings, to such journals as might ask for them.

The following papers were presented by Edward Hart: " Not on Some Curious Specimens of Zinc Oxid" ; " Note on a Bariun Blast Furnace Slag."

He explained that some granulated zinc having been acci dentally left in an earthenware crucible in a muffle over night, le to the discovery of a most curious formation of zinc oxide, an having designedly repeated the experiments, the results wer exhibited.

The barium blast furnace slag was from Nova Scotia. Th ore contained 6.30 per cent. barium sulphate, and the slag 3.4 per cent. barium oxide, as the chemist of the company reporte it. The question was referred to Prof. Hart how to calculat the barium in the slag, and from the data which he gave he con cluded it was neutral, the barium sulphate being reduced t barium sulphide, and existing as such in the slag.

Prof. Richards called attention to the notable amount of alu minum, *viz.*, sixty-three per cent. in the pig iron produced a the furnace mentioned. He cited a case of a furnace in the Ju niata Valley, which, under abnormal conditions had produced as high as one per cent. aluminum, although, as is well known, the presence of metallic aluminum in pig iron is considered in admissible by some authorities.

Mr. Colby suggested that hereafter a topic be chosen for the

evenings discussion, and a leader be appointed to open the discussion and it was decided to adopt the plan at the next meeting.

ALBERT H. WELLES,
Secretary.

NEBRASKA SECTION.

A meeting of the Nebraska Section was held on Thursday, Dec. 19, in the Chemical Laboratory of the University of Nebraska. The meeting was a pronounced success in every way.

The following papers were read: (1) "The Occurrence of Native Iron in Nebraska," by Prof. H. H. Nicholson." (2) "The Effect of Freezing on the Salts in Solution in Spring and Well Waters. Preliminary Notice," by Prof. H. H. Nicholson. (3) "The Description of a Shaking Apparatus for Laboratory Use," by Mr. R. S. Hiltner.

RHODE ISLAND SECTION.

The December meeting of the Rhode Island section was held at Providence on Thursday evening, December 12, 1895, Chairman, Mr. C. A. Catlin presiding.

Dr. J. C. Hebden read a paper upon "The Relation of Acid and Basic Properties of the Artificial Dyes to their Dyeing Properties."

The paper was illustrated with diagrams and dyed samples of wool.

The January meeting was held at Providence, Thursday evening, January 16, 1896, C. A. Catlin in the chair.

A paper upon "Amphoteric Reaction of Milk" was read by W. M. Saunders. After mentioning the results obtained by various investigators upon the subject, the reader described the experiments performed by himself. The milk of about seventy-five cows was examined as to the reaction to litmus paper. The larger number gave a neutral reaction to litmus, the remainder an acid or alkaline reaction in about equal proportion. Cows giving milk with an alkaline reaction to litmus on one day gave the acid reaction a few days later.

CINCINNATI SECTION.

The Section met in regular session Wednesday, January 15, 1896, President Twitchell presiding.

Mr. F. Homburg, chairman of the committee appointed to draft resolutions on the death of Prof. C. R. Stuntz, reported the following:

"Since it has pleased Providence to call from his labors to rest, Prof. C. R. Stuntz, we, the members of the Cincinnati Section of the American Chemical Society, through our committee, desire to express our deep sorrow at the loss of our esteemed friend and colleague, and also our sincere sympathy with all who mourn his death.

"His genial disposition, his courteous bearing, his devotion to science and learning in general, and to the success of our organization in particular, we keenly appreciate.

"The legacy of his noble example will tend to alleviate the distress caused by his departure.

"F. HOMBURG,
"DR. S. P. KRAMER,
"E. TWITCHELL,
"H. B. FOOTE,
"Committee."

On motion of Dr. Springer, the resolutions were adopted, and the committee was instructed to send a copy to the family of the deceased.

Mr. H. B. Schmidt, of Cincinnati, was elected a member of the Section.

Papers were read on "Mercury: Its Occurrence and Production," by Frank I. Shepherd; and "A Few Notes on the Determination of Lead," by J. Hayes-Campbell.

Issued with March Number, 1896.

Proceedings.

COUNCIL.

The following persons have been elected as members of the standing committees for one year:

Committee on Papers and Publications—J. H. Long and Thomas B. Osborne.

Committee on Nominations to Membership—A. A. Breneman, P. T. Austen, and C. A. Doremus.

Finance Committee—Durand Woodman, A. P. Hallock, and A. H. Sabin.

C. F. Mabery has been elected a member of the Council for 1896 in place of Charles B. Dudley, President.

The bills of the Chemical Publishing Co. for $289.24 for the January number and $272.43 for the February number of the Journal, have been approved.

NEW MEMBERS ELECTED FEBRUARY 1, 1896.

Bookman, Samuel, 9 East 62nd St., N. Y. City.
Fullam, Frank L., cor. Gold and John Sts., Brooklyn, N. Y.
Hanks, Abbot A., 718 Montgomery St., San Francisco, Cal.
Lihme, I. P., 27 Tift Ave., Cleveland O.
Lippincott, Warren B., 3179 Ashland Ave., Chicago, Ill.
Maywald, F. J., 592 Kosciusko St., Brooklyn, N. Y.
Lerch, Fred., Virginia, St. Louis Co. Minn,
Sharpless, Fred. F., 811 Wright Black, Minneapolis, Minn.
Stearns, F. C., M.D., 44 Montgomery St., Jersey City, N. J.

ASSOCIATE ELECTED FEBRUARY 1, 1896.

Gordon, Alexander, 44 Montgomery St., Jersey City, N. J,

NEW MEMBERS ELECTED FEBRUARY 24, 1896.

Baker, Theodore, Box 97, Belford, N. J.
Barrett, Jesse M., Purdue University, Lafayette, Ind.
Borland, Chas. R., E. C. Powder Co., Oakland, Bergen Co., N.J.
Cheney, John P., So. Manchester, Conn.
Christiansen, H. B., Hermitage, Floyd Co., Ga.
Jones, Wm. J., Jr., Purdue University, Lafayette, Ind.
Martin, Alex. M., F.C.S., Douglas Villa, Dunbeth Road, Coatbridge, Scotland.

Myers, H. Ely, Riddlesburg, Bedford Co., Pa.
Slagle, Robert Lincoln, Brookings, S. D.
Smyth, Dr. Geo. A., 900 South Boulevard, Oak Park, Ill.
Tidball, Walton C., care of E. R. Squibb & Sons, Gold and John streets, Brooklyn, N. Y.

ASSOCIATES ELECTED FEBRUARY 24, 1896.

Pomeroy, Thomas W., Lafayette College, Easton, Pa.
Stover, Edward C., Trenton Potteries Co., Trenton, N. J.

CHANGES OF ADDRESS.

Atkinson, Elizabeth A., Three Tons, Pa.
Baekeland, Leo., care Nepera Chem. Co., Nepera Park, N. Y.
Blalock, Thos. L., 3106 O'Donnell St., Baltimore, Md.
Bromwell, Wm., Ph.D., care Tenn. C. I. and R. Co., 1918–1920 Morris Ave., Birmingham, Ala.
Campbell, Geo. F., 80 Bristol St., New Haven, Conn.
Chamberlain, G. D., care N. W. Mall Iron Co., Milwaukee, Wis.
Cornelison, R. W., care McKenzie Bros. & Hill, Bloomfield, N. J.
Doremus, Dr. C. A., 17 Lexington Ave., N. Y. City.
Foote, Henry B., 241 Walnut St., Cleveland, Ohio.
Graves, W. G., 1661 Huron St., Cleveland, Ohio.
Kenan, Wm. R., Jr., care Carbide Mfg. Co., Box 45, Niagara Falls, N. Y.
Kiefer, H. E., 16 W. 4th St., South Bethlehem, Pa.
Morse, Fred. W., Lock Box 30, Durham, N. H.
Spencer, G. L., Centralia, Wood Co., Wis.
Trubek, M., 325 Academy St., Newark, N. J.
Walker, Henry V., 38-40 Clinton St., Brooklyn, N. Y.

ADDRESS WANTED.

Johnson, Jesse, last address Augusta, Ga.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The regular monthly meeting of the Washington Section was held December 12, 1895, President Munroe in the chair, with thirty-six members present. In the absence of the Secretary, W. D. Bigelow was elected Secretary, *pro tempore*. The following were elected to membership: W. W. Skinner, F. B. Bomberger, and H. Carrington Bolton. A committee was appointed

to arrange for a social meeting of the Section to report at the January meeting.

The first paper of the evening was " Exhibition of Argon and Helium," by Dr. W. F. Hillebrand. He discussed concisely the spectra of argon and helium and closed by exhibiting the spectra to the Society.

The second paper was by Dr. H. W. Wiley, on the " Use of Acetylene Illumination in Polariscope Work, with Illustrations." Dr. Wiley stated that acetylene, while not inferior in point of accuracy to other forms of illumination, is so intense as to permit accurate polarization with solutions so dark in color that they cannot be polarized with lights commonly used for this purpose. He called attention to the " Schmidt and Haensch Triple Field Polariscope," which was said to be a great assistance in both rapid and accurate work. The paper was illustrated with the acetylene light and the polariscope referred to.

Mr. F. P. Dewey read a paper on " The Early History of Eletric Heating for Metallurgical Purposes." The paper was comprehensive, embracing the various patents relating to electric heating for metallurgical purposes and also many relating to electric reduction. It was illustrated by photographs and drawings of the various forms of apparatus described.

The last paper of the evening was " A Tribute to the Memory of Josiah P. Cooke," by Dr. Marcus Benjamin. An excellent portrait of Prof. Cooke was exhibited and the sketch of his life was of special interest from the fact that the statements made were from a manuscript sent to Dr. Benjamin some years ago by Prof. Cooke. After discussion by Messrs. Munroe, Tassin, and Wiley, the Section adjourned.

NEW YORK SECTION.

The regular meeting of the New York Section was held at the College of the City of New York on Friday evening, Feb. 7, at 8.30 P. M. The following papers were read : New Facts about Calycanthus," by Dr. R. G. Eccles, and " Items of Interest from the Cleveland Meeting," by A. A. Breneman.

Dr. Eccles described his work and also that of Dr. H. W. Wiley on the calycanthus seeds and the alkaloids obtained

therefrom ; exhibiting the seeds, the principal alkaloid obtained, its salts, the color reactions of both, and the crystalline forms of the salts.

Prof. Breneman described the features of the Cleveland meeting, which were of particular interest to industrial chemists, referring especially to the low pressure distillation of light petroleum oils as conducted in Prof. Mabery's especially equipped laboratory.

Dr. Durand Woodman exhibited a simple lecture table apparatus for experimentally demonstrating the luminosity of the acetylene flame, generating the gas from calcium carbide.

The meeting was adjourned at 10.45 P. M.

ANNUAL REPORTS OF THE SECTIONS.

The following annual reports from the secretaries of the sections were received by the General Secretary too late for insertion in their proper place :

WASHINGTON SECTION.

Seven meetings have been held and an abstract appended gives the list of papers read and topics discussed at these meetings. The following is a list of the present officers :

President—Charles E. Munroe.

Vice Presidents—E. A. de Schweinitz and W. D. Bigelow.

Treasurer—W. P. Cutter.

Secretary—A. C. Peale.

The officers as above with the following constitute the Executive Committee : H. W. Wiley, F. P. Dewey, F. W. Clarke, and W. H. Seaman. There are no other standing committees.

The secretary of the local section has no way of determining the standing of members. According to a statement made by the General Secretary, December 8, 1894, the membership of the Washington section was sixty-four. As it now appears to be seventy-four the gain during the year is ten.

November 8, 1894.—President W. H. Seaman in the chair. Ten members present. Resignation of Prof. J. C. Gordon read and accepted. Cooperation of the Society asked by John W.

Hoyt in the formation of a " National Post-Graduate University." Prof. H. W. Wiley made a report on the " First Congress ot Chemists," at the San Francisco exposition. Paper read by W. D. Bigelow on the " Coloring-Matter in California Red Wines."

December 13, 1894.—President W. H. Seaman in the chair Twenty members present. Paper by Oma Carr and J. F. Sanborn on the " Dehydration of Viscous Organic Liquids," read by Mr. Carr. Mr. W. D. Bigelow and E. E. Ewell described a continuous extractor for large quantities of material.

January 10, 1895.—President W. H. Seaman in the chair. Fourteen members present. The following officers were elected: President Charles E. Munroe; Vice Presidents, E. A. de Schweinitz and W. D. Bigelow; Treasurer, W. P. Cutter; Secretary, A. C. Peale. Additional members of the Executive Committee, H. W. Wiley, F. P. Dewey, F. W. Clarke, and W. H. Seaman. H. C. Sherman, F. P. Veitch, W. G. Brown, and V. K. Chesnut were elected to membership.

February 14, 1895.—The meeting was devoted to the annual address of the retiring president, W. H. Seaman, upon " Chemistry in Education." President Charles E. Munroe in the chair, with members of the Society ane invited guests from the Societies of Washington present.

March 14, 1895.—President Charles E. Munroe in the chair. Thirty-five members present. Dr. J. E. Blomén and G. E. Barton elected to membership. The following papers were read: " The Constitution of the Silicates," by F. W. Clarke. " On the Chloronitrites of Phosphorus and the Metaphosphinic Acids," by Dr. H. N. Stokes; " The Manufacture of Soluble Nitrocellulose for Nitrogelatin and Plastic Dynamite," by Dr. J. E. Blomén.

April 11, 1895.—President Charles E. Munroe in the chair. Fifty-three members present. The following papers were read: " The Determination of Nitrogen in Fertilizers," by H. C. Sherman; " Exhibition of Calcium Carbide," by Charles E. Munroe; " Precipitation of Small Quantities of Phosphoric Acid by Ammoniacal Citrate of Magnesia," by E. G. Runyan and H. W. Wiley. The Subject for discussion was " Can Argon be Accepted

as a New Element?" Discussion was by Charles E. Munroe, F. W. Clarke, T. M. Chatard, and H. N. Stokes.

May 9, 1895.—President Charles E. Munroe in the chair. Forty members present. Messrs. Marion Dorset and S. C. Miller elected to membership. The following papers were read: "A New Meteorite from Forsyth Co., N. C.," by E. A. de Schweinitz; "Hydrogen Fluoride Poisoning," by Peter Fireman; "Progress in the Manufacture of Artificial Musk," by W. H. Seaman. The subject for discussion was "The Chemical Action of Micro-organisms," and was participated in by E. A. de Schweinitz, Surgeon-General Sternberg, H. W. Wiley, Prof. George P. Merrill, and R. B. Warder.

The Society adjourned until November.

CINCINNATI SECTION.

The annual election held December 18th, 1894, resulted as follows:

President, Karl Langenbeck; Vice-Presidents, B. D. Westenfelder and I. J. Smith; Treasurer, Henry B. Foote; Secretary, E. C. Wallace; Directors, Dr. S. P. Kramer, Prof. O. W. Martin, H. L. Nickel.

The following were elected chairmen of the standing committees for the year:

Didactic, Physical, and Inorganic Chemistry, Dr. Alfred Springer.

2. Organic Chemistry, Prof. T. H. Norton.

3. Analytical Chemistry, Lewis William Hoffmann.

4. Medical, Physiological, and Biological Chemistry, Dr. S. P. Kramer.

5. Technical and Pharmaceutical Chemistry, Prof. J. U. Lloyd.

The following named persons have been elected members of this Section since October 31, 1894: W. G. Wallace, Richard W. Proctor, Charles E. Jackson and George F. Feid, elected December 18, 1894; F. Homburg, E. D. Frohman, elected January 15, 1895; Harry L. Lowenstein, elected Febuary 15, 1895; Prof. A. F. Linn, and Dr. John McCrae, elected October 15, 1895.

In the death of Lewis William Hoffmann and W. G. Wallace

the Cincinnati Section sustained a loss of two of its popular younger members, who were highly esteemed by their associates.

Eight meetings were held during the year, at which the following papers were presented. Special meeting held November 7, 1894, addressed by Dr. H. Hensoldt. The subject announced, "Occult Science in the Orient."

Stated meeting December 18, 1894: "Diphtheria Antitoxin," Dr. S. P. Kramer; "Elective Fermentation in Diabetes," Dr. Alfred Springer.

Stated meeting January 15, 1895: "Separation of the Solid and Liquid Fatty Acids," E. Twitchell; "Report of Progress in Organic Chemistry," Dr. H. E. Newman.

Stated meeting February 15, 1895: Papers announced were postponed on account of sickness of the essayists. "The Difficulty of Obtaining Distilled Water to Meet Pharmacopeial Requirements," was discussed by Prof. Lloyd, Dr. Springer, and Prof. Norton.

Stated meeting March 15, 1895: "Determination of Phosphorus in Ferrosilicon," John H. Westenhoff; "The Souring of Milk," Robert W. Hochstetter.

Meeting April 16, 1895: "Recent Important Discoveries in Chemistry," Prof. T. H. Norton.

Meeting May 15, 1895: "Adulteration of Powdered Elm Bark," Henry B. Foote; "Ammonium Thioacetate," Prof. T. H. Norton.

Stated meeting October 15, 1895: "A Tribute to Pasteur," Dr. Alfred Springer; "Laboratory Uses of Aluminum and Recent Progress in Theoretical Chemistry," Prof. T. H. Norton.

A pamphlet issued by the Executive Committee gives names, occupation and addresses of members of the Section, the names of the authors and titles of papers read during 1894.

NEBRASKA SECTION.

The Nebraska Section was organized at a meeting held in Lincoln, June 14, at which meeting officers were elected for the ensuing year, as follows:

President, H. H. Nicholson; Secretary and Treasurer, John

White; Executive Committee, H. H. Nicholson, John White, Rosa Bouton, T. L. Lyon, W. S. Robinson.

The first regulnr meeting of the Section was held in the Chemical Laboratory of the University of Nebraska on October 30, with a good attendance of members and a number of invited guests.

Papers were read as follows:

By Prof. T. L. Lyon: "The Source of Error in the Estimation of Sugar in Beet Juice by Means of the Sucrose Pipette."

By Mr. Samuel Avery: "Notes on the Electrolytic Determination of Iron, Nickel and Zinc."

Mr. C. H. Suveau, of the Department of Motive Power of the Burlington and Missouri River Railroad, was elected a local associate member.

Other meetings will be held in December, March and June.

Our present membership is thirteen.

CHICAGO SECTION.

The Chicago Section has held but two meetings, one for organization, and the other just reported, at which papers were presented.

The membership is twenty-five.

The officers are as follows:

President, Frank Julian; Vice-President, J. C. Foye; Secretary, F. B. Dains; Treasurer, J. H. Long; Executive Committee, Frank Julian, A. L. Smith, F. B. Dains.

NEW YORK SECTION.

Meetings were held and papers read as follows:

November 9, 1894: "The Rapid and Accurate Analysis of Bone-black," by William D. Horne; "Recent Progress in Physiological Chemistry," by Dr. E. E. Smith.

December 13, 1894: The Chemical Nature of Diastase," by Thomas B. Osborne, of New Haven; "Glucose from a Sanitary Standpoint," by E. H. Bartley, M.D.; "Indiscriminate Taking," by P. T. Austen.

January 10, 1895: "Improvement in the Manufacture of Acetone," by Dr. E. R. Squibb; "Recent Progress in Photographic Chemistry," by Dr. J. H. Stebbins.

February 18, 1895: No quorum.

March 8, 1895: "The Late Prof. Henry B. Nason," by W. P. Mason; "Elective Fermentation in Diabetes," by Alfred Springer; "Note on Absorbent Blocks," by W. H. Broadhurst; "Note on the Precipitation of Iron by Alkali Nitrites," by Gillett Wynkoop; "Volumetric Determination of Zinc and Manganese and a New Indicator for Ferrocyanides," by G. C. Stone; "Note on the Reduction of Nitrates by Ferrous Hydroxide," by P. T. Austen; "Stability to Light of Haematoxylin Blacks on Wool," by P. T. Austen.

May 11, 1895: "Recent Progress in Analysis of Soils," by H. W. Wiley; "Tribute to the Memory of Dr. Gideon Moore," by C. F. McKenna; "Chemical History of Caase of Arsenical and Antimonial Poisoning," by C. A. Doremus; "The Estimation of Acetic Acid in Vinegar," by A. R. Leeds.

June 14, 1895: "Determination of Nitrogen by the Gunning Method," by W. D. Field; "On Asbestos and its Commercial Application," by G. C. Stone; "Examination of Lard for Impurities," by David Wesson; "On Commercial Argol and its Products," by Wm. McMurtrie; "A Modern View of Electro-Chemical Action," by C. L. Speyers; "On the Relation of the Chemical Engineer to Factory Management," by John Enequist.

The informal dinners preceding the meetings have been continued at a majority of the meetings. The total expenditures of the section have amounted to $157.98; those of the preceding year were $160.82. The largest item in each case is the contribution to the Treasury of the Scientific Alliance.

The following officers have been elected for the current year; Chairman, P. T. Austen; Secretary and Treasurer, Durand Woodman; Executive Committee, A. H. Sabin, A. C. Hale, A. R. Leeds; Delegates to Council of Scientific Alliance, P. T. Austen, C. F. McKenna, A. C. Hale.

The list of members is annexed hereto, and shows a total membership of 234 as compared with 183 last year, or a gain of fifty-one members.

RHODE ISLAND SECTION.

The Rhode Island Section of the American Chemical Society

respectfully transmits the following general report of the business of the Section for the year September 1, 1894, to September 1, 1895.

The work of the Rhode Island Section for the past year may be described in brief as follows, all the meetings having been held in Providence:

September 27, 1894: A paper prepared by Prof. E. E. Calder upon the "Chemistry of Albuminurea," was read by Mr. W. M. Saunders, the author being unable to be present.

October 18, 1894: A paper was read by Mr. W. M. Saunders upon "Lantern Slides and their Preparation," illustrated by the stereopticon.

December 13, 1894: A paper was read by Charles A. Catlin, upon "Bread and Bread Stuffs."

January 17, 1895: A paper was read by Mr. Geo. F. Andrews upon "The Accuracy of the fire assay of Silver."

February 23, 1895: A paper was read by Prof. J. H. Appleton upon "Argon."

March 21, 1895: A paper was read by Mr. J. P. Farnsworth upon "Selection of water for Bleaching and other Manufacturing Purposes."

April 24, 1895: A paper was read by Mr. C. H. Burgess upon "A Resumé of the methods of Bleaching Cotton Piece Goods."

May 23, 1895: A paper was read by Mr. E. D. Pearce upon "The Coloring-Matter of Pollens," with illustrations under the microscope.

June 13, 1895: The annual meeting was held at the Hope Club House where the members were entertained at dinner as the guests of the Chairman, Mr. Charles A. Catlin, who presented a paper upon "Chemical-Laboratory Microscopy," illustrated by the microscope.

The interest in the local section still continues to be well sustained, and already another new year of its work has begun with very flattering prospects for the future.

At present date the names of the officers of the Section are: Chairman, Charles A. Catlin; Secretary and Treasurer, Walter M. Saunders; Executive Committee, Chairman, ex-officio, Secretary and Treasurer ex-officio, George F. Andrews.

Number of members belonging to the Rhode Island Section at the present time, twenty (20). Net increase over last year two (2).

LEHIGH VALLEY SECTION.

It has been found desirable, as the Section is limited in number, to hold fewer meetings. Four meetings have been held during the past year; *viz.*, November 1, 1894, January 17, May 2, and October 10, 1895. The October meeting was the most successful in the history of the Section, the Society entertaining at that time Thomas Tyrer, Esq., President of the Society of Chemical Industry of England, and invited representatives of the New York Section of the same Society and the New York Section of the American Chemical Society. An inspection of the large government plant of the Bethlehem Iron Co. was made, followed by an elegant dinner tendered the visiting chemists, while the stated meeting was held in the afternoon at Lehigh University.

The following papers have been presented: "Helmholz's Contributions to Science," George P. Scholl; "Castner's Electrolytic Process for Production of Caustic Soda," W. H Chandler; "A New Ammonia Condenser," Edward Hart; "The Determination of Graphite in Pig Iron," P. W. Shimer; "The Selection of Samples for Analysis," A. L. Colby; "On standardization of Iodine Solution," G. H. Meeker; "A Device for Sampling Metals," P. W. Shimer; "The Rapid Methods Used in the Bethlehem Iron Co.'s Laboratory," A. L. Colby.

Mention should also be made of the interesting paper read by Dr. William McMurtrie at the October meeting, on "Chemical vs. Bacteriological Examination of Water," written by Prof. W. P. Mason.

We close the year with the same number as we began, *viz.*, 21, losses having been made up by new members.

Our annual meeting will be held the third Thursday in January. The officers of the Section for the year 1895 are as follows:

Presiding Officer—Edward Hart.

Treasurer—Albert L. Colby.

Secretary—Albert H. Welles.

Executive Committee—Edward Hart, Albert L. Colby, Albert H. Welles, and J. W. Richards.

THE CLEVELAND EXCURSIONS.

Owing to delay in the receipt of copy it was impossible to give a full account of the meeting at Cleveland in last month's issue. The following additional matter has since been received by the editor:

One very pleasing feature of the meeting in Cleveland was the excursions to various works and other places of interest. Both afternoons were set apart for this purpose, one special party made a trip on Tuesday morning, and on Monday evening the Case School of Applied Science and Adelbert College were visited. Such a large number of excursions were planned, and so many works were freely opened for inspection, that it was impossible to visit them all. Routes Nos. 1, 6, and 7, as given by the local committee's program, were omitted, and all the time available was devoted to the others.

Route No. 2 was led by Mr. D. B. Cleveland, chemist of the American Wire Works.

The first place visited was the plant of the Otis Steel Co. Mr. Bartol, the Superintendent, took charge of the visitors and showed them the plate mill, the basic open hearth furnaces, the steel foundry, the car axle foundry, the machine shop and the laboratory.

The Continental Chemical Co. was next visited. They make red pigments and fuming sulphuric acid from copperas, but had unfortunately been recently burned out, so that it was impossible to see the works.

The manager, Dr. Ramage, exhibited an apparatus for making ozone, which he said brought its cost down to such a point as to warrant its being used for disinfecting garbage, refuse from stock-yards, fats, etc.; for bleaching, for oxidizing sulphurous to sulphuric oxide, thus doing away with the lead chambers in the manufacture of sulphuric acid, and for many other purposes.

He claimed that treatment with ozone is an almost sure cure for consumption in the first two stages and for syphilitic diseases.

He stated that with one-fifth to one-seventh of a horse power he can change one hundred and twenty cubic feet of atmospheric air a minute to a mixture containing fifteen to eighteen per cent. of ozone, all the oxygen present being changed. He uses a fifty volt and two to three ampere alternating current, which he converts to a current of fifty thousands volts.

The Cleveland Nitrous Oxide Co. was next visited, and Mr. Clark and Mr. Hatch showed the party around.

They sell oxygen and hydrogen, epsom salts, liquid nitrous oxide and carbonic acid gas. They also make nitrate of ammonia, as the commercial salts is to impure for their use.

They exhibited some acetylene gas burning from an ordinary gas jet to show the character and illuminating power of this much talked-of new illuminant.

By this time it was too late to visit other places of interest, and the party returned to the hotel.

Route No. 3 was taken on Tuesday morning, the members of this party thus missing the regular morning session. This was done at the suggestion of the Managers of the Varnish works, as their work of boiling varnish could only be seen in the morning. The party was guided by Mr. George Marshall, and included the following places: Cleveland Varnish Co., Cleveland Rubber Co., Glidden Varnish Co., and Warner & Swasey, instrument makers.

A party of six started Tuesday at 9 A. M. from the Hollenden and proceeded to the Cleveland Varnish Co., where Mr. Stark, the chemist, conducted them through the works and explained the different processes. The store-room was first visited, wherein large boxes of rosin are stored, some from New Zealand and some from Zanzibar, the first-named place being the chief source. The gums or rosins used for varnish are amber, fossil and annual; amber and fossil are best, as the thousands of years they have lain in the ground seems to have cured them. These gums are assorted according to color, the lightest being the most valuable. They are found by probing in the sand, in lumps from the size of a bean to that of a wash tub. The largest piece of Kauri gum found weighs 250 pounds. This is the chief gum, but Zanzibar is also used for fine varnishes. These gums are insoluble

in common solvents or oil, and must be melted at 560° F. in order to decompose partially, so that they may unite with the oil. The chemists visited the boilers where the operation of dissolving the gum was in progress. These boilers are large vessels, in shape somewhat like the farmer's sap or soap kettles, placed on a small buggy to facilitate removal from the fire. From twenty to twenty-five per cent. is driven off as water and non-drying oils on heating. The latter are unstable, and have not been investigated or utilized, except in connection with the lampblack industry. The gums are prepared for the boilers by hand, as the best size for melting (about that of a hen's egg), is obtained by chopping with a small hatchet. The machines crush them too fine. Linseed oil does not dry quickly unless boiled, and dryers are made by adding a lead or manganese salt to boiled oil. These combine with the oil, forming a compound which absorbs oxygen quickly and hardens. The boilers for oil are the same as for melting, generally larger, with hoods to carry off volatile products. The gum boilers are fitted with covers to decrease loss from spattering and to control the irritating fumes which are carried off by means of tall chimneys. Different solvents, as turpentine, for instance, are used to give required consistency to the finished varnish, and are added to the cooled mixture formed by adding boiled oil to the melted gum. The varnish is then allowed to settle in large tanks for from two months to as many years. The longer the time the finer the varnish made. This is necessary, as filtering does not remove the sediments. The top is siphoned off, filtered through filter presses and run into tanks for ageing. The ageing room is kept at a constant temperature, such that the varnish is fluid for from nine to eleven months. The party visited the cooper shop, storage tanks, shellac mixers, (which are nothing more than a barrel fastened on a shaft to rotate in the direction of its circumference), and a paint mill of the latest pattern, which does not materially differ from the earliest ones made. The filters were of the well known Johnson's make, and the cloths may be used one day, then removed and agitated in a shellac mixer with turpentine until the gummy sediment is washed out. Each lot of varnish, japan, or enamel after ageing

is tried, *i. e.*, some substance for which it will eventually be used as a cover, is coated with it and dried or baked.

The most noticeable feature at the Varnish Co., sets aside the old adage about the shoemaker's wife and blacksmith's colt, for paint and varnish had been used in a very neat and tasty manner throughout the establishment, and what was particularly prominent, was the absolute cleanliness that pervaded even the store-rooms, the settling and ageing rooms where long lines of tastefully painted tanks pleased the eye, and the excellent arrangement of drafts, hoods, covers and stacks to carry off the offensive odors detrimental to the workman's health.

After visiting the laboratories and drying rooms, the offices were next in order, where a most pleasant surprise was in store. At the invitation of the president, Mr. Tyler, the chemists sat down to a most elaborate luncheon, which was very acceptable. After a vote of thanks had been given their hospitable host, the visitors wended their way to the Cleveland Rubber Co.

Notwithstanding the torn up condition of the rubber company on account of inventory, every courtesy was shown by the foreman of each department, who personally explained his part of the work. The first room visited was the calendering room, where the crude exudings of the South American rubber trees are mangled into workable shape. The rubber gum as received contains fourteen to eighteen per cent. water, and ten to twelve per cent. extraneous matter, such as stones, twigs, bark, etc. Stones are the favorite adulterants, as the crude gum is bought by weight. The gum is first run through rollers upon which water plays, to cleanse it. It comes from the rollers looking like a sheet of thin cork. It is then allowed to cure for three or four months in a dry room at about 70° F. The South American natives cure rubber by exposure to air and sun, so that vulcanization is not necessary, and they make very durable shoes from the product so cured. Modern science has not yet perfected a system for hastening this curing operation, and it is necessary to cure at 70° three or four months since higher heat has a decomposing effect. From the curing room the rubber is passed through slightly heated rollers again and again until it becomes a compact, yielding, non-porous mass. A little vaseline added

in this working serves to make the mass more pliable and softens it. From the first rollers it passes to others, where different colored powders are added and worked into the body of the rubber. Pure rubber is black and is useless for many purposes, but by mixing with various constituents it may be impressed into the pores of cloth, making a covering impervious to moisture, rolled into sheets capable of holding gases or liquids, moulded into any shape, hardened by heat, and welded. The fillers, as they are called, are zinc oxide, whiting, lampblack, litharge, sulphide of iron and antimony, and many other substances known only to the trade. Each filler has a different effect on the rubber. Sulphide of antimony is used for fine elastic rubber, such as is used in dental operations and for marine valves. In general, if rubber is to be hardened, as when used for door mats, or if the surface is made impervious to moisture or air for gas bags, water bottles, mackintoshes, hose, bicycle tires, etc., sulphides are used in order that vulcanization may take place after the article is formed. Litharge, lampblack and zinc oxide give color as well as body to the rubber. In order to cover cloth the rubber is wound on rollers and fed through calenders or heated rolls set to such a size that rubber introduced between the rolls in mass is forced through the cloth and becomes part of it; at the same time, by heating the rolls vulcanization also takes place. Vulcanization consists of forming a compound of sulphur and rubber in air by heating, and although it takes much of the elasticity from the rubber, renders it impervious to liquids or gases. Cloth was shown prepared in this way for mackintoshes, hose, etc. Cloth so prepared may be sewed together; a solution of rubber in any volatile solvent applied to the stitches, or the seam covered with a strip of rubber wet with this solution, the whole placed in a steam-heated oven, heated and when withdrawn it is found the cement has welded the holes left by stitches, or the strip upon the original pieces so that it becomes a compact mass.

The party next visited the molding department. Here the rubber is prepared as above with a filler of some sulphide and then pressed like dough into heated molds. It is very plastic, filling all crevices readily and taking every impression. It does

not melt, but first heat softens it to the consistency of soft taffy, while a greater heat vulcanizes it. In order to keep surfaces in contact from welding together, a little whiting is sprinkled between them. Scraps are reworked, and old rubber, such as boots, is reclaimed and made into coarse articles, such as mats. The mechanical arrangements were (some of them) wonderful, but space cannot be given to a detailed description of them all. As the time for the morning excursion had now been expended, the party were obliged to forego the pleasure of visiting the other places of interest on the list.

It is to be regretted that more did not avail themselves of the opportunity extended to them to visit these works.

Route No. 4 was for convenience, divided into two excursions, the Grasselli Chemical Works being visited on Tuesday and the other places on Monday.

The trip to the Oil works was under the guidance of Mr. H. L. Payne, chemical engineer, and the visitors were introduced to the practical side of a subject, whose chemical side was so interestingly presented by Dr. Mabery in his address on the same evening. Only one refinery was visited.

The one selected is not under the control of the Standard Oil Co., and works up all of its own product. The visitors were therefore fortunate in being able to see within the confines of one muddy hillside all the branches of this vast industry. The members of this firm, Messrs. Scofield, Shurmer & Teagel, were all very obliging, and Mr. Daniel Shurmer and his son personally conducted the party through the extensive works.

The stills are sheet steel tanks set in brick work and have an open coal fire under them. Some are set on end and others lie on the side. They are not usually covered in like a boiler, but exposed to the air on top and sides, and only protected from the weather by a rough shed. This circumstance would seem to cause a waste of fuel, but it probably assists in the proper "cracking" of the oil. The distillate is condenced in a series of wrought iron pipes, which are kept cool by immersion in a long wooden trough. The trough is kept filled with cold water from springs in the side hills. Various methods of procedure are adopted in the distillation, depending upon the character of

the product desired, for not all of the various oil products are or can be made in one distillation. The lighter and more volatile products are usually collected together and then redistilled with steam heat in order to separate them into commercial "naphtha," "benzine," "gasoline," etc. In this distillation the steam is introduced directly into the oil and the condensed water is drawn off at the bottom of the still-tank. The very light vapors and gases which come off first are sucked down by a steam syphon and burned under the boilers.

The residue left in the crude oil stills may be either a thick tarry pitch or the distillation can be carried so far that only a porous coke is left. This coke contains only 0.01 to 0.02 per cent. ash, and is in great demand for the manufacture of electric-light carbons.

The burning oils are all purified by washing in a huge lead-lined separatory funnel, called an agitator. They are first washed with concentrated sulphuric acid which unites with and precipitates the basic matters, such as phenol. The oil after this washing contains less oxygen than before. The principal object of this treatment is to remove those bodies which would cause a coloration of the oil; a water-white kerosene is supposed to best suit the consumer. The excess of acid is washed out with water or steam and the oil is completely neutrallized by a little caustic soda. The refinery is using some Lima oil, and they treat it with litharge in the agitator to remove the sulphur. Other refineries use copper oxide in their stills for the same purpose.

One of the most interesting products of crude oil is paraffin. It distills over as a greenish oil, and the visitors were permitted to examine the crystallizing process where the solid wax is frozen out and filtered from the more liquid part of the oil. A second or third tereatment of the crude wax with solvent naphtha and this freezing process, turns out the pure white chewing gum. Every paraffin works has its own ammonia freezing plant.

Most of the refineries have no chemist in their employ. They are mainly concerned with the physical properties of their products, and a boy soon learns to make the test for specific gravity, flashing point, burning point, freezing point and viscosity.

The cooperage and shipping departments were large and interesting, but when the party arrived at that portion of the works they were ready to return to the hotel.

The other excursion of Route No. 4 was taken by all on Tuesday morning. The Grasselli Company's works are of such magnitude that a description is impossible. They make sulphuric acid, nitric acid, hydrochloric acid, mixed acid for nitroglycerol factories, ammonia, glycerol, and all the various salts and bye products of such an industry. Mr. E. F. Cone, chief chemist of the experimental laboratory, was the conductor on this occassion, and Mr. C. A. Grasselli, president, and his staff of superintendents were instrumental in showing everything in the works. None of the chemists will forget the pleasant little lunch which awaited them in the company's office.

Route No. 5 was of interest to iron works chemists, and comprised the Cleveland Rolling Mill and the Blast Furnace department and mill of the Union Rolling Mill Co. It was in charge of Mr. F. E. Hall.

The party left the Square at 1:30 P.M. Monday and proceeded first to the Cresent Sheet and Tin Plate Co.'s Works on Bessemer Avenue, near the N. Y. P. & O. R. R. This company employs two hundred men and has a capacity of thirty tons per day of sheet iron and tin plate. The plant is new, having been in operation about one year, and is fitted up with all the latest improvements in boilers, engines and all machinery, including an electric plant for lighting, and operating the electric cranes for handling rolls and heavy materials.

From here the party proceeded to the Emma Blast Furnace at the intersection of the N. Y. P. & O. and C. & P. Railroads. This furnace is operated by the Union Rolling Mill Co., whose rolling mills were visited later. The furnace department employs one hundred men and has a capacity of two hundred tons of pig iron daily. The plant is modern in every respect, has three blowing engines and three brick hot blast stoves. The company's chemical laboratory is located at the furnace plant and is in charge of Mr. Frank E. Hall.

The next place visited was the rolling mill of the same company, situated some distance farther up the C. & P. R. R. Here

are employed about 350 men, the daily produced of the works being about 150 tons of merchant iron. No steel is made, the company making a speciality of high grade wrought iron.

After inspecting this plant the party proceeded to the large works of the Cleveland Rolling Mill Co. This works is the largest in the city. The Bessemer Steel plant has a capacity of 1,000 tons daily, about seventy-five per cent. of which is made up into finished products, consisting of rails, shafts and wire, in the various departments of the company's works. In all about 3,500 men are employed.

One blast furnace is located at this plant. The company's two larger furnaces are located about three miles farther down on the N. Y. P. & O. R. R., from which place "direct metal" is run to the converters, the molten metal being carried this distance over the N. Y. P. & O. R. R.

The chemical laboratories of the company are in charge of Mr. Chaddock. Ten chemists are employed.

Route No. 8, Adelbert College and Case School of Applied Science were appointed for Monday evening. Dr. Gruener, instructor of chemistry in Adelbert College, was absent on his vacation, and Mr. H. L. Payne, a graduate of the first chemistry class in Case School, was appointed to head this excursion.

The new physical laboratory of Adelbert College exicited the greatest admiration. The chemical laboratory lacked its most interesting feature—Dr. E. W. Morley.

At Case School the visitors saw the marks of an active and well equipped institution for the study of practical applied science. The entertainment of the evening, of course, was Dr. Mabery's talk on "Petroleum."

Route No. 9 was to the Steel Works at Lorain, O. The trip was in charge of Mr. Hugo Carlsson, chief chemist of the Johnson Co.

These works occupy about eighty-six acres of land lying along the Black river, two miles south of Lorain. The plant was first put in operation April 1, 1895. Their finished products are billets and special rails for street railways. The plant consists of the Bessemer department, blooming mill, shape mill, engine and boiler houses, etc. Plans for the erection of six blast fur-

naces have been completed and work will begin on the erection soon.

The engine house contains the blowing engine for the Bessemer department; this was made by the Southwark Company, Philadelphia. It is a horizontal double expansion engine with blowing cylinder sixty inches diameter and sixty inches stroke. In the same building are the dynamos and straight line engines which furnish power for the Johnson Electric Railway between Lorain and Elyria. There are two boiler houses containing National Water Tube Boilers with Murphy Automatic Stokers, the combined capacity of the two batteries being about 6,000 horse power. The feed water is heated and purified before it enters the boilers. Gas for the heating furnaces is furnished by a plant of Duff gas producers. Four ten-foot cupolas melt the pig metal, and there are two eight-foot cupolas for spiegel. The converting department contains two ten ton vessels. Ingot molds are arranged on small cars in pairs. There is no casting pit. The ingots are transferred from the converter house to the soaking pits, in which they are kept until ready for rolling. The blooming mill is driven by a very powerful reversing engine, built by the Galloways, Manchester, England. It has double cylinders each fifty-five by sixty inches. The shape mill is driven by two engines, also of the Galloways' make. The heating furnaces are provided with two cranes, one for charging and one for drawing.

An important feature of the works is the special machinery for straightening rails. The laboratory occupies a two-story brick building, and contains a 250,000 pound Olsen testing machine.

THE RECEPTION BY THE CHAMBER OF COMMERCE.

The various hosts who had vied with one another in extending courtesies and hospitalities to the visiting chemists while in Cleveland, not being satisfied with the royal welcome which they had already given, tendered their guests a most delightful reception in the rooms of the Chamber of Commerce, Tuesday evening, Dec. 31. We quote from a Cleveland paper the following description of the elaborate decoration of the rooms:

"The decorations were to a certain extent paradoxical, being

emblematic of both summer and winter. The walls of the ceiling were draped with holly, heavily laden with red berries. This drapery came down to within a few feet of the floor, where it was met by banks and screens of palms and other tropical plants. This apparent paradox was a pretty tribute to the various sections of the country, north and south, from which the guests came.

The floral designs added to the beauty of the scene. One, a large shield of white, studded with roses, bore the following inscription:

'Welcome, 1895—American Chemical Society.'

In the center of the assembly room, on a table, stood an immense design which was a tribute to Dr. E. W. Morley and took the form of a reference to his great genius in determining the atomic weight of oxygen. It was a huge balance erected on a base of American beauty roses. From the arms of the balance hung globes of white flowers. On one in purple was the simple capital letter 'O,' representing oxygen, and on the other the purple figures '15.879,' the atomic weight of oxygen."

On entering the Chamber the guests were welcomed by the Reception Committee, and introduced to the Cleveland gentlemen who were present. From early in the evening until midnight the visiting chemists had the pleasure of meeting in social intercourse those who had already done everything in their power to welcome and entertain the American Chemical Society, and to furnish them opportunities for a successful meeting.

During the evening the Chamber of Commerce Musical Club and the Schubert Mandolin Club rendered various choice selections, which were enthusiastically received. The evening was also enlivened by the humorous recitations and impersonations of Mr. J. E. V. Cooke.

Refreshments were served during the evening in the committee room, and it seemed as though nothing was wanting to make the occassion one long to be remembered. To cap the climax, however, and to show their appreciation of one of Cleveland's most distinguished scientists, a message of greeting and complimentary reference to his labors in determining the atomic weight of oxygen, was sent by cable to Dr. E. W. Morley, who is spending the winter in Europe.

Some of the chemists were obliged to leave on early trains and were thus unable to enjoy the whole of the evening. But they, as well as those who remained, took with them the pleasantest recollections of their visit to Cleveland, and the Twelfth General Meeting of the American Chemical Society.

Erratum.—Page 32, sixth line from bottom of page *for* sixty-three per cent. *read* sixty-three hundredths of one per cent.

Issued with April Number, 1896.

Proceedings.

COUNCIL.

The Council have approved the nomination of Edward Hart as Editor for 1896.

CHANGES OF ADDRESS.

Bloomfield, L. M., 1239 Harrison Ave., Cleveland, Ohio.
Furman, H. Van F., Room 118, Boston Building, Denver ,Col.
Koebig, Dr. Julius, 306 Market St., San Francisco, Cal.
Pemberton, H., Jr., 1008 Clinton St., Philadelphia, Pa.
Phillips, Francis C., P. O. Box 126, Allegheny, Pa.
Sherman, H. C., Columbia University, New York City.
Spencer, G. L., 134 Rich Ave., Mt. Vernon, N. Y.

ADDRESSES WANTED.

Bachman, Irving A., formerly of Augusta, Ga.
Jones, Dr. Walter, formerly of Lafayette, Ind.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The annual meeting was held January 9, 1896. and was called to order by the President, Charles E. Munroe, at 8:00 P. M.

The following persons were elected to membership : Messrs. E. W. Magruder, C. C. Moore, and E. C. Wilson.

The publication of Bulletin No. 9 was announced and arrangements reported by a committe for a social meeting to be held in February.

The reports of the Treasurer and Secretary were read and adopted, after which the election of officers for the ensuing year was held with the following result :

President—E. A. de Schweinitz.

Vice-Presidents—W. D. Bigelow and W. G. Brown.

Treasurer—W. P. Cutter.

Secretary—A. C. Peale.

Additional Members of the Executive Committee—Charles E. Munroe, V. K. Chesnut, F. P. Dewey, and H. N. Stokes.

The first paper of the evening was read by H. W. Wiley on a "Steam-Jacketed Drying Oven." "In order to surround the drying space of an oven entirely with steam, the door of an ordinary steam-jacketed drying oven is made with double walls, into which the steam from the oven is conducted by two metal flexible tubes inserted at the top and bottom of the door. They are so arranged as not to interfere with opening the door. By this method the entire drying space of the apparatus is surrounded with steam, easily securing a constant and even temperature.

"The temperature is regulated by a pressure gauge in which the steam, by acting on a column of mercury, cuts off the gas when a given pressure is reached. A steam pressure of two inches will cause a temperature of about 102° in the drying space of the oven. By setting the gauge at any position desired, the temperature can be regulated, when steam is used, to read from the boiling-point of water up to 105°. For other temperatures other liquids can be used. For instance, alcohol, or amyl alcohol for still higher temperatures, and so on. Ether cannot be employed with safety on account of the danger of explosion in case of leakage."

Dr. Wiley exhibited the drying oven in actual operation.

The second paper, also by Dr. Wiley, was on the "Heat of Bromination of Oils." "The method of determining the heat of bromination of oils, as proposed by Hehner and Mitchell, in a recent number of the *Analyst*, is very difficult to work from the meager directions given by the authors. The especial difficulty in the process is in handling the liquid bromine in quantities of one cc. at a time. I find that the process is made practicable by dissolving both the oil or fat and the bromine in chloroform, in which condition the bromine solution is easily handled by means of a special pipette.

"In order to make a number of analyses of the same sample, five grams of the fat may be dissolved in chloroform and the volume completed to fifty cc. Ten cc. of this solution will contain one gram of the fat. In like manner five cc. of bromine may be dissolved in chloroform and the volume completed to fifty cc., or larger quantities in the same proportion may be used. The

gradual evolution of hydrobromic acid from a mixture does not interfere with the analytical process, as the amount of bromine used is always largely in excess. Ten cc. of the bromine solution containing one cc. of the liquid bromine are used for each ten cc. of fat solution.

"The pipette for handling the bromine solution is so arranged as to be filled by the pressure of a rubber bulb, thus avoiding the danger of sucking the bromine vapor into the mouth. The solution is poured upon the chloroform solution held in a long narrow tube, in which a delicate thermometer, capable of being read to tenths of a degree, by means of a magnifying glass, is placed. This tube is held in a large cylinder, from which the air can be removed, thus affording a good insulation in respect to heat.

"The determinations should be conducted in a room where the temperature is as constant as possible and the pieces of the apparatus should be exposed to the open air for at least half an hour after completing one determination before beginning another, in order to be restored to the standard room temperature. Duplicates usually agree within one or two-tenths of a degree, though sometimes the variations are greater.

"The ratio of the heat of bromination to the ordinary number must be established for each system of apparatus employed. The heat of bromination of various oils was determined by the method and apparatus described above, and the process seems to be one of considerable analytical value. For exact scientific purposes, calorimetric measurements of the degree of heat produced must be made."

Discussion was by Messrs. Warder, Freeman, and Munroe.

Professor Charles E. Munroe then made some remarks upon the "Corrosion of Electric Mains." He exhibited sections of electric light cables in which the lead coating had become so corroded that in some places the interior conductor was exposed, while at others the cable was coated with nodular earthy-looking masses. The cables were parts of and arranged on the three wire system, which carried a direct current of 110 volts on each wire, and which had been laid underground in the upper compartment of a terra cotta conduit. The corroded main was a branch in an alley. The principal main in the street was not

attacked in the least. Analysis showed the incrustation to contain nitrate, chloride, carbonate, oxide of lead, water, and a trace of organic matter. Surrounding the alley were stables, and the author found in the salts in the soil produced by the excreta all the necessary materials and conditions for effecting chemical corrosion *per se*, without resorting to any electrolytic theory.

Dr. Wiley, in discussing the paper, said he thought there might have been a denitrifying process.

Professor Munroe said there could have been no constant moisture present, that is, there was no submergence, but there must have been water passing through the conduit.

CINCINNATI SECTION.

The section met in regular session Saturday evening, February 15, 1896. Vice-President Martin presided.

Dr. Alfred Springer read a paper on "The Characteristics of Illuminates," and exhibited a photograph of the bones of the hand made by means of the Roentgen X rays. The picture was kindly loaned for the purpose by Mr. G. W. Zwick, of Covington, Ky., who had recently brought it from Germany.

"Notes on Helium and Argon" was read by Professor T. H. Norton.

Dr. S. Waldbott showed how the value of litmus paper as an indicator could be enhanced. His method was to use a capillary pipette instead of an ordinary stirring rod, and to hold the point of the pipette containing a drop of the solution upon the litmus paper; a bright red spot would be seen at the point of contact, even in very dilute acid solutions. The Doctor's paper on "The Assay of Ipecac," announced for the evening, was postponed till next meeting.

NORTH CAROLINA SECTION.

On February 22nd about a dozen chemists met in the office of the Experiment Station in Raleigh to organize the North Carolina Section. The following officers were elected:

President—F. P. Venable, University of North Carolina, Chapel Hill.

Vice-President—Charles E. Brewer, Wake Forest, N. C.

Secretary and Treasurer—W. A. Withers, Raleigh, N. C.

The following papers were read :

" Absorptive Power of the Soil for Bases and Its Relation to Fertility," by Prof. Withers.

" A Study of the Zirconates," by Dr. Venable and Mr. Clark.

" Notes on the Reduction of Methylenedi-*o*-*p*-*m*-nitraniline," by Dr. Baskerville.

NEW YORK SECTION.

The regular meeting of the New York Section was held at the College of the City of New York, on Friday evening, March 6th, at 8:30 o'clock, Professor P. T. Austen in the chair.

The following papers were read :

" The Cassel-Hinman Gold and Bromine Process," by P. C. McIlhiney."

" The Specific Gravity of Glue Solutions," by E. R. Hewitt.

" Investigations in the Chemistry of Nutrition," by Dr. W. O. Atwater.

Mr. McIlhiney enumerated the advantages of bromine over chlorine in the gold extraction process as (1) greater solubility of bromine, as three and two-tenths per cent. against 0.76 per cent.; (2) lesser oxidizing power, whereby the iron pyrites is less acted upon ; (3) greater solvent power for gold.

The bromine is recovered by distillation with live steam in stone tanks, after addition of sulphuric acid and an oxidizing agent.

The process is especially adapted to low grade telluride ores, which have not hitherto been profitably worked.

Mr. Cassel, being present, was asked to what extent the process had been worked, and whether ores containing sulphides could be treated. He replied that fifty tons *per diem* had been treated since January 1st, and the capacity was to be increased; that ores containing small amounts of sulphides had been successfully treated, using very weak solution of bromine, and eighty per cent. of the bromine had been recovered ; but it was best to roast sulphide ores. The cost, including roasting, was $1.75 per ton.

Mr. Hewitt, in his work on the " Specific Gravity of Glue Solutions," had obtained his results from experiments on all grades of glue from the best photographic gelatine, to the darkest and poorest grades in the market.

He found the expansion of glue solutions to be the same as water alone; that the specific gravity of glue containing water was less than in the dry state; that the hydrometer could not be used in solutions containing over sixty-five per cent., and that the quality of the glue had no effect on the specific gravity of the solutions.

He concludes that there is a series of distinct chemical combinations of glue with water.

In the discussion of the paper, Dr. Horne asked if the specific-gravity of a glue solution could be determined by dropping it into some solution of known density, not acting on the glue solution.

Mr. Hewitt replied that this method had been tried, using xylol, chloroform, and some other liquids, but the results were not as satisfactory as could be obtained by the hydrometer.

The presence of Dr. C. B. Dudley, president of the society, was then announced, and Dr. Dudley addressed the meeting in part as follows:

"*Gentlemen of the New York Section:* It has been a rare pleasure to attend this meeting of the New York Section, and I would like to congratulate you on one or two points. First, the advantage that comes to you from being able to meet together, read papers, shake hands, and dine together. I am so far away from the chemists that it does me good to meet and shake hands with a chemist. In the early days of the Pittsburg Society I tried to meet with them and have been present on many enjoyable occasions, but having joined the society when there was only a New York Section, I have felt at home with you and have wished I could meet with you oftener.

"Another thing on which I wish to congratulate you. Our General Secretary informs me that we have a good round thousand now in our membership. There are those of you who have stood by the society when it was not as prosperous as it is now, who can appreciate this.

"Now as to what is to be done in the field of our labors. My daily work, or a great part of it, is with iron and steel, and if I could, I would give all my time to the study of pig iron.

"There are many problems yet to be solved in regard to it,

and of which a great deal might be said, but as there are other papers to come before you this evening, I will not detain you longer. I am very glad to have been able to meet with you."

Dr. W. O. Atwater was then introduced, and after giving a synopsis of the work which had been done in other countries, especially in Germany, on the chemistry of food and nutrition, he described the progress which had been made in this country, beginning with the early work of Professor Baird, then of the Smithsonian Institute, who gave the first impulse to this work by his studies of the food value of a number of varieties of fish. He then passed to a description of the work recently done under his direction and that now in progress in determining the heats of combustion, or fuel values of food. He said that we know the laws of conservation of energy hold good in the living organism, but we do not yet know *how* they hold good. We must study these things in the living organism, and for this paper a respiratory calorimeter has been constructed at Middletown by which the experimental determination of heat of radiation, energy of food consumed, etc., is to be obtained. A man had been kept in this apparatus for four days, and it was expected to arrange to extend the experiment to a week or even several weeks.

Eight attendants were required to run these experiments.

Dr. Dudley asked whether Professor Atwater had used a current of oxygen instead of potassium chlorate in his experiments on the heats of combustion of foods, and stated that he had used the oxygen with very satisfactory results in determinations of calorific value of coal.

Dr. Dudley also asked whether the quality of the fat of animals was dependent on the food.

Professor Atwater replied that the fat formation is a function of both the organism and the food.

On motion of the secretary, a vote of thanks was passed to Professor Atwater for his interesting report on the progress of the chemistry of nutrition.

Professor Breneman moved that a committee be appointed to make a report at the next meeting on the feasibility of organizing a chemical club from the members of the New York Section. Seconded and carried.

The Chair appointed Messrs. Breneman, McMurtrie, and Hallock.

The Librarian announced the receipt of a bequest from Dr. A. A. Fesquet, of two microscopes and accessories. The Chair directed that a suitable recognition of the gift be made.

RHODE ISLAND SECTION.

The regular meeting of the Rhode Island Section was held at Providence, Thursday evening, Feb. 13, 1896. Mr. Chas. S. Bush in the chair.

A paper was read by Mr. Charles E. Swett. Subject, "Ultramarine."

The reader presented the results of a few experiments he had performed upon ultramarine, with some of the more common reagents.

The March meeting was held on the 19th inst., at Providence. Chairman C. A. Catlin, presiding.

Mr. Walter E. Smith read a paper upon "The Origin of Petroleum."

In brief, the paper was as follows:

The theories given for the origin of petroleum are in general divided into three classes:

1. The chemical theories advanced by Berthelot and Mendeléeff, that water on metallic carbides forms acetylene, which is further changed.

2. The theory that it is indigenous to the rocks in which it is found.

3. The theory that it is a distillate formed from highly organized substances.

Proceedings.

COUNCIL.

The Council has decided to hold the summer meeting at Buffalo, August 21 and 22.

NEW MEMBERS ELECTED MARCH 26, 1896.

Brown, Thomas, Jr., M.S., Princeton, N. J.
Danner, W. E., 441 Green St., Philadelphia.
LaWall, Charles H., 305 Cherry St., Philadelphia.
Nagelvoort, J. B., 3237 Michigan Ave., Chicago, Ill.
Sprout, Louis P., Scotia, Pa., P. O. Benore.
Stewart, Dr. Andrew, 1420 Q St., N. W., Washington, D. C.
Wagner, John R., Drifton, Pa.

ASSOCIATES ELECTED MARCH 26, 1876.

Caldwell, Thomas O., Agr. Exp. Sta., Bozeman, Mont.
Flowers, John, Agr. Exp. Sta., Bozeman, Mont.
Pilgrim, Heber B., Lafayette College, Easton, Pa.
Sieb, Peter, Agr. Exp. Sta., Bozeman, Mont.
Twitchell, Mayville W., 709 8th St., N.E., Washington, D.C.
Walter, Charles Albert, 506 South 5th St., Champaign, Ill.

CHANGES OF ADDRESS.

Barton, G. E., care Whitall, Tatum & Co., Flint Glass Works, Millville, N. J.
Benjamin, Dr. Marcus, Smithsonian Institute, Washington, D. C.
Berry, W. G., 26 Whitehall St., N. Y. City.
Breyer, Theo., P. O. box 112, Peoria, Ill.
Brown, H. F., 113 West Central St., Natick, Mass.
Fields, J. W., Stillwater, Okla.
Johns, John, 306 Toone St., Baltimore, Md.
Kelley, J. H., 26 Snell Hall, Univ. of Chicago, Chicago, Ill.
Lloyd, Rachael, care R. L. Lloyd, Lansdowne, Pa.
Low, A. H., P. O. drawer 1537, Denver, Colo.
Maury, George P., care Edgar Thompson Steel Works, Braddock, Pa.
Nickel, Herman L., care N. K. Fairbank Co., St. Louis, Mo.
Pomeroy, Charles T., 190 Mt. Pleasant Ave., Newark, N. J.
Rosengarten, F. H., care Photographic Society, 10 So. 18th St., Philadelphia, Pa.
Steiger, Geo., 1425 Corcoran St., N.W., Washington, D. C.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

A regular meeting was held February 13th, 1896. As the meeting was devoted mainly to social purposes and the inauguration of the newly elected president, Dr. E. A. de Schweinitz, it was held at the rooms of The Washington Down Town Lunch Club. After the transaction of necessary business a lunch was served which was enjoyed by thirty-one members. The following persons were elected to membership: Clinton P. Townsend, S. S. Voorhees, and Dr. F. K. Cameron.

The Presidential address before the Washington Section was delivered by the retiring President, Professor Charles E. Munroe, at a special meeting held Friday, February 21, the subject being "The Development of Smokeless Powders." The lecturer sought to show that the necessity for a high-power, smokeless propellent had been created by the mechanical perfection to which ordnance had attained and the precision of the weapons and the instruments by which they were directed; that the possible production of such propellent was dependent on the discovery of guncotton, nitroglycerol, and certain nitro-substitution compounds, and the improvements in their manufacture; that the possibility of producing uniform and reliable propellents was dependent on the invention of pressure gauges and velocimeters; and that the possibility of their economical production was dependent on the invention of mechanical mixers and formers applied in other arts. In a historical résumé it was shown how very recent most prior inventions and discoveries were, and it was pointed out that a very large proportion of the inventions were made by American scientific men.

The many smokeless powders manufactured or prepared were then described or enumerated and classified into mixtures of different cellulose nitrates with oxidizing agents; mixtures of soluble or insoluble cellulose nitrates with oxidizing agents; mixtures of soluble or insoluble cellulose nitrates with nitroglycerol; mixtures of cellulose nitrates with nitro-substitution compounds; and pure cellulose nitrate powders; and the methods of manufacture were briefly stated.

The lecturer then related his own experience in inventing a smokeless powder. Recognizing at the outset the necessity for the closest approximation to absolute chemical and physical uniformity in a high-powered powder, and being familiar with the difficulty of securing such constancy in a physical mixture, he set about producing a powder from carefully purified cellulose nitrate of the highest degree of nitration. This was the first and only attempt made, so far as the lecturer was aware, to produce a powder which consisted of a single substance in its pure state.

A factory was erected at the Torpedo Station, prior to his resignation of his position there, and the powder manufactured was proved at Indian Head by Ordnance Officers of the Navy. Secretary Tracy said of this powder, "Report of the Secretary of the Navy, 1892, page 25." "It became apparent to the Department early in this administration that unless it was content to pass behind the standard of military and naval progress abroad in respect to powder, it must take some steps to develop and to provide for the manufacture in this country of the new smokeless powder, from which extraordinary results had been obtained in Europe." With this object negotiations were at first attempted looking to the acquisition of the secret of its composition and manufacture. Finding itself unable to accomplish this the Department turned its attention to the development of a similar product from independent investigation. The history of these investigations and of the successful work performed in this direction at the Torpedo Station has been recited in previous reports. It is a gratifying fact to be able to show that what we could not obtain through the assistance of others we succeeded in accomplishing ourselves, and that the results are considerably in advance of those hitherto obtained in foreign countries."

The conditions that a smokeless powder should fulfill and the tests prescribed by the lecturer were then set forth, and in closing he pointed out that the powder was now developed to a higher degree than the gun and that changes in the latter to render it more efficient were being considered by ordnance experts.

CINCINNATI SECTION.

The Section met in regular session, Tuesday, March 17, 1896. President Twitchell presided.

The discussion of "The Scientific Concepts of Etidorhpa" was announced for the evening. The popularity of the book was evidenced by the presence of many friends of the author and of the other members of the Section.

Dr. Alfred Springer read extracts from the book and took issue with the author on some of the statements. Prof. Lloyd re-affirmed his belief in the theories advanced and referred the Doctor to the preface to the author's edition, in which he had stated he would decline "to make any subsequent comments on the work." The Professor then read three chapters in the original manuscript, which had been omitted from the published work. He now regrets the omission, as the continuity of the narrative is somewhat impaired thereby.

RHODE ISLAND SECTION.

The regular meeting of the Rhode Island Section was held at Providence, Thursday evening, April 16, 1896, Chairman, Charles A. Catlin, presiding.

Mr. Charles S. Bush read a paper on "Petroleum Products." The following is an outline of the paper:

1. Discovery of petroleum.

2. Brief history of the petroleum industry in the United States.

3. Outline of the distilling and refining process now in general use in the United States.

4. The importance of petroleum as a means of reducing friction to a minimum.

5. New methods compared with old ones, especially referring to "petroleum products" used for lubricating purposes.

NEBRASKA SECTION.

The regular meeting of the Nebraska Section was held at the University of Nebraska, on Tuesday evening, March 31, at eight o'clock.

The president being absent, Mr. Samuel Avery was elected chairman *pro tem.*, and called the meeting to order.

The following papers were read :

"Recent Work on the Röentgen Rays," by Prof. D. B. Brace, of the Department of Physics, University of Nebraska.

"Report on Argon," by Miss Rosa Bouton.

"Calcium Carbide and Acetylene," by Dr. John White.

Prof. Brace exhibited some Crookes' tubes prepared in his laboratory, made a general statement of the manner in which these were prepared and used, of the effect of the X or Röentgen rays, and exhibited some photographs taken by their use. Of these one was of special interest; it represented a shadograph of a metal object taken by the cathode and anode rays. There was no appreciable distinction between them.

Miss Bouton's paper gave a very thorough and clear account of argon, from the very earliest experiments of Lord Rayleigh on the density of nitrogen down to and including the present state of our knowledge of argon, its chemical and physical properties.

Dr. White exhibited a specimen of calcium carbide, which had been prepared in the electrical laboratory of the University, gave a brief historical statement of the carbides in general, and of their use in the preparation of acetylene. He then prepared some acetylene by treatment of the carbide with water, and by burning the gas under proper conditions showed how it may be used as an illuminant. He followed this by a short lecture, in which the economic use of acetylene as an illuminant was dealt with, laying special stress upon its advantages and disadvantages.

Owing to the lateness of the hour, Dr. White's paper on "Metallic Suboxides" was postponed.

At the business meeting which followed, Mr. E. C. Ellioet and Miss Marietta Gray were elected members of the Section.

NEW YORK SECTION.

Minutes of the meeting of April 10.

A report was made by the chairman of the committee appointed

to consider the organization of a chemical club in New York. Out of eighty-two replies already received, sixty were unconditionally in favor of the project.

It was further stated that as there had evidently been some misunderstanding as to the intended membership, it should be known that there is no intention of limiting the membership to any section of the chemical fraternity, but to include chemists and chemical manufacturers generally.

Dr. Albert R. Leads read a paper on "Standard Prisms in Water Analysis, and the Valuation of Color in Potable Waters."

In the discussion of Dr. Leed's paper, Prof. Birchmore explained an arrangement of adjustible colored prisms projecting inside a glass cylinder, one over the other, by which the Nessler reagent colors could be matched and recorded. The cylinder is to be filled with a liquid having the same refractive index as glass; oil of juniper was mentioned as suitable; and the record is made by readings on the milled heads of the screws by which the overlapping of the prisms is regulated.

Dr. Leeds moved that a committee be appointed to unify the methods of color comparison and report upon a standard of measurement of color in potable waters.

Prof. McMurtrie thought that such committee should be appointed by the council, and that the secretary should communicate the resolution to the President of the Society.

Dr. Leeds' motion, as amended by Prof. McMurtrie, was seconded and carried.

A paper was read by C. L. Speyers on "Matter and Energy."

Dr. E. G. Love exhibited some fine photomicrographs of starches.

Dr. L. Saarbach exhibited and described an improved form of "Laboratory Temperature Regulator," which he had found sensitive, reliable, adjustable, and easily taken apart for cleaning.

Issued with June Number, 1896.

Proceedings.

COUNCIL.

Prof. H. H. Nicholson, Lincoln, Neb., has been elected a member of the Council, to take the place left vacant by the election of Dr. C. B. Dudley to the presidency of the Society.

The Council has voted to accept the invitation to hold the winter meeting at Troy, N. Y., on Tuesday and Wednesday, December 29 and 30.

The New York Section has asked that a committee be appointed to unify the methods of color comparison and report on a standard for measurement of color in potable waters. The Council has agreed to the formation of such a committee and named the following persons to act as members: A. R. Leeds, Wm. P. Mason, Thomas M. Drown.

NEW MEMBERS ELECTED MAY 11, 1896.

Bowman, J. W., Green Island, N. Y.
Hunziger, Dr. Aug., care Weidman Silk Dyeing Co., Paterson, N. J.
Yates, J. A., Williamsburg, Ky.

ASSOCIATES ELECTED MAY 11, 1896.

Meade, Richard K., Longdale, Va.
Pilhashy, Benjamin M., 1058 Cutter St., Cincinnati, O.

CHANGES OF ADDRESS.

Dodge, F. E., 316 Bowne Ave, Flushing, N. Y.
Hays, Joseph A., 147 So. 18th St., Pittsburg, Pa.
Hopkins, Cyril G., 409 W. Main St., Urbana, Ill.
Lord, N. W., 338 W. Eighth Ave., Columbus, O.
Peale, A. C., box 2043, Station A, Philadelphia, Pa.
Power, Frederick B., 535 Warren St., Hudson, N. Y.
Shepherd, Frank I., Kyle, Ohio.
Stillwell, J. S., box 3015, N. Y. City.
Tonceda, Enrique, care Troy Steel Co., Troy, N. Y.

ADDRESSES WANTED.

Gallaher, Phil. C., formerly of Leadville, Colo.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The regular meeting of the Section was held Wednesday evening, April 15th.

Dr. S. Waldbott presented a paper on "The Assay of Ipecac," in which he outlined the various methods for the alkaloidal assay of crude drugs and gave some results obtained by applying the Lloyd method for the assay of fluid extracts, to the determination of emetine in ipecac root; with some slight modification, Dr. Waldbott thinks good results may be obtained.

In a paper on "The iodoso- and iodo-compounds and iodonium bases, Dr. John McCrae gave an interesting account of some of the work he had done on these compounds, under the instruction of Victor Meyer.

NEW YORK SECTION.

The New York Section held its usual monthly meeting in the chemical lecture room in the College of the City of New York on Friday evening, May 8, with about fifty members present, Dr. Peter T. Austen, presiding. In response to inquiries regarding the progress made by the committee appointed to canvass the matter of the organization of a chemical club, Prof. Austen stated that in accordance with the instructions given, it had increased its numbers to fifteen and had held several meetings, to one of which the members of the New York sections of the American Chemical Society and of the Society of Chemical Industry, as well as manufacturers and gentlemen interested in the science and art of chemistry, business men and friends of chemistry were invited. The meeting was full and enthusiastic. The committee was instructed to increase its number to fifty or more and to push the organization of the club as rapidly as possible. The committee had held another meeting and added a large number of names of prominent chemists, manufacturers, and business men to the list. The general opinion seems to be that the initiation fee should be fixed at $25, and yearly dues at $25. It is the intention, while in no way hampering or restricting the evolution of the Chemical Club, which many of the more enthusiastic supporters of the movement predict, to start the club in a conservative and economical way, and not to exceed

the pecuniary limit which shall be decided upon after careful deliberation. It appears that there is not in existence in this or any foreign country any real chemical club, as differentiated from a chemical society. It is believed that the science and art of chemistry furnish so much that is characteristic that a chemical club may easily be made a unique organization. The members of the committee of fifteen are Prof. A. A. Breneman, Dr. A. P. Hallock, Prof. Peter T. Austen, Dr. W. McMurtrie, Prof. Morris Loeb, Prof. C. A. Doremus, Dr. E. R. Squibb, Dr. J. H. Wainwright, Mr. A. H. Mason, Mr. S. W. Fairchild, Mr. W. H. Nichols, Mr. W. J. Matheson, Mr. T. F. Main, Prof. A. H. Sabin, and Dr. C. F. Chandler.

Dr. A. R. Leeds, of Stevens Institute, read a paper on the "Bacteria of Milk Sugar." The author finds that the morphology, classification, physiology, and botany of bacteria are so rudimentary and unsatisfactory that the most valuable methods of bacteriological investigation are still of a chemical nature, and the advances to be made in the near future are to be looked for mainly on the chemical sides of the subject.

The author was interested to note in the progress of his work that precipitated zinc hydroxide, which is generally considered amorphous or gelatinous, is really crystalline.

Dr. H. W. Wiley, of the United States Department of Agriculture in Washington, offered a paper entitled "Recent Advances in Milk Investigations." In the absence of the author the paper was read by Dr. William McMurtrie. It treated of the bacterial theory of milk decomposition, the composition of woman's milk as compared with cow's milk, and the relative value of the two for infant food, and of the commercial standards which should be fixed for the milks sent to the city markets.

The author reviewed the work of Söldner regarding the proteid content of human milk, and quoted the figures given by authority for the average composition of human milk, as follows:

	Per cent.
Proteids	1.52
Fat	3.28
Sugar	6.50
Ash	0.27
Citric acid	0.05
Undetermined	0.78
Total dry substance	12.40

The undetermined substances, 0.78 per cent., are mostly nitrogenous bodies not generally found in cow's milk, and for this reason cow's milk can never be so diluted or altered as to properly supply the natural nutriment of the infant.

Söldner follows the method of Munk for determination of proteids, regarding as non-proteid matter those nitrogenous bodies not precipitated by tannin in presence of common salt. In woman's milk these amount to nine per cent. of the total nitrogenous constituents, and in cow's milk to about six per cent.

The author then discussed the view of Bechamp that milk derived from healthy animals is capable of spontaneous alteration, which consists in the development of lactic acid and alcohol and the development of curds in those milks which contain caseinates produced by the precipitating action of the acids formed. Oxygen and the germs present in the air are held to have nothing to do with this alteration of the properties of milk. The general conclusion reached is that microorganisms, such as vibriones and bacteria, are developed by a natural evolution from the microzymes, even in milk which has been boiled.

The surprising results of Söldner and Bechamp should lead to new studies of bacterial action in milk. If it should prove true that milk contains autogenetic germs for its own change, and that by the development of these germs into vibriones and bacteria, the natural souring takes place, it will be necessary to change completely the common view respecting these processes.

The author further discussed the commercial standards for the composition of milk, declaring that the value of milk, both for butter and cheese making, should be gauged by its content of butter fat, denouncing the claim of dealers that any milk from a healthy cow should be sold without legal restriction, no difference what its content of fat may be, and recommending that the minimum standard for fat content of milk supplied for human consumption should be placed at three per cent. or higher.

Dr. Leeds considers that in judging of the figures of Söldner presented it is important to be informed of the conditions under which the samples for analysis were taken and the quantity used for analysis, particularly for the determination of such constituents as citric acid and the undetermined substances. Samples

of woman's milk usually available are too small for such minute determinations. Regarding the content of proteids, the figures of Söldner do not vary widely from those previously found and reported. One hundred samples of woman's milk examined in New York gave an average of less than two per cent., with variations of 0.75 per cent. to 4.75 per cent. The only explanation of the very low figure of Söldner is that only partial secretion was available. The figure 1.52 given is not surprising.

That the various bodies secreted from the blood should be present is generally accepted. Variations in the composition of the milk, due to emotional influences, such as nervousness, excitement, fatigue, fright, anger, etc., are well known.

The fat and total solids given in the analysis are surprisingly low.

Dr. Eccles questioned the declaration that modified cow's milk was not a proper food for infants. Constant experience, forced by necessity, shows that it supplies excellent nutrition for infants.

Prof. Marston Bogert, of Columbia College, read a paper on "Normal Heptyl Thiocyanate."

The steps followed by the author in preparation of heptyl thiocyanate are as follows: Production of heptyl alcohol from oenanthol by reduction with zinc dust and acetic acid, conversion of the heptyl alcohol into the bromide, and addition of the bromide to boiling alcoholic solution of potassium thiocyanate. The yellow oil finally obtained washed free from potassium thiocyanate, dried with calcium chloride and distilled, all passed over between 230° and 234° C.

Normal heptyl thiocyanate is a colorless, mobile liquid, having a slightly alliaceous but rather pleasant odor and a specific gravity of 0.931 at 15° C.

Dr. Austen exhibited an apparatus for lecture demonstration of the properties of the heavier gases.

WASHINGTON SECTION.

A regular meeting was held Thursday, March 12th, 1896, with President Dr. de Schweinitz in the chair. There were

thirty-five members present, and Dr. Andrew Stewart was elected to membership.

Mr. F. P. Dewey read a paper on "The Refining of Lixivating Sulphides." Dr. Dewey's paper reviewed the leaching process and the treatment of sulphide precipitates produced. He described the sulphuric acid process of treating the sulphides, in which they are treated in strong sulphuric acid to convert the sulphides into sulphates, after the charge is treated with water, the silver precipitated by copper and melted, the copper sulphate crystallized. In the 1894 run of the Marsac Refinery, 116,519¼ pounds of sulphides, carrying 572,544.4 ounces of silver by the corrected assay were treated, and 574,623.26 ounces of silver were returned, showing a plus clean up of 2,073.81 ounces, or 0.36 per cent. 96.29 per cent. of the product was in the form of bars, averaging 999.4 fine in silver, no gold.

Professor H. W. Wiley and E. E. Ewell read a paper[1] on "The Determination of Lactose in Milks by Double Dilution and Polarization."

Professor H. Carrington Bolton read a paper on "Berthelot's Contributions to the History of Chemistry," reviewing his "Collection des Alchimistes Grecs," (Paris, 1887; 3 Vol. 4to), and his "La Chimie an Moyen Age," (Paris, 1893; 3 Vol. 4to), showing their scope, analyzing their contents and indicating the important changes in chemical history resulting from Berthelot's studies.[2]

In the discussion of Dr. Bolton's paper, Dr. Wiley referred to the fact that the Phoenicians, as early as 1200 years before Christ, became famous by reason of the remarkable dyes which they produced, and that they were derived from a colorless substance found in certain mollusks, which, when exposed on fibers to the light, turned green, then red and purple. He referred to the fact that on the continent of Europe many scientific men had also become famous in politics, and among them preëminently Berthelot and Virchow. Berthelot was at least one official chemist who had attained political distinction, and his career might be imitated with advantage to the public service by some

[1] This Journal, 18, 428.
[2] This Journal, 18, 466.

American scientists; and we should not despair of looking forward to the day when chemists should at least be members of the Cabinet, if not Presidents of the United States. He thought Berthelot was particularly well suited to write of the alchemists, because some of his views would do credit to the wildest vagaries of the alchemists, especially his notion that the art of the chemist in the synthesis of foods, would in the near future render the practice of agriculture unnecessary. But we should not criticise a great man because of his vagaries, and after all it may be true that insanity is the highest type of genius.

The topic of discussion for the evening was "Style in Chemical Books and Papers." Dr. Wiley opened the discussion by saying there are many problems that present themselves to authors of scientific work. Some of these are of vital importance, while others are mere matters of taste. Not having expected to discuss the question on this occasion, he would confine himself to the minor topics. He suggested that there should be some uniform systsm of abbreviation employed, and for his part preferred very much small letters without periods. The introduction of capital letters in abbreviations marred the appearance of a book, and appeared to be entirely unnecessary. He thought perhaps some abbreviation of common metric terms would prove advantageous; for instance, the writing of the words cubic centimeters repeatedly not only requires a great deal of space, but the repetition of the term becomes tiresome. Some short word might be used to represent this magnitude, as, for instance, cubics. It would be well for chemists to agree upon some such system, provided the system were rational and easy of application.

Another question which often arises is in regard to the agreement between the noun and the verb, as, for instance, should we say 100 grams of iron are, or 100 grams of iron is? Another minor point is in the writing of numerals; whether they should be written out or the Arabic numerals used. He has adopted the plan of writing out in full numbers below 100, and placing the Arabic numerals for 100 and above. This was an arbitrary division, however, which might well be changed if some agreement could be reached in regard to it.

It appears that most scientific writers are so eager to express the truth or fact which they wish to convey that they lose sight altogether of the style in which the expression is made, and, as a result, their sentences become involved, and their meaning far from clear.

Another point which merits discussion is in the use of proper names to indicate any apparatus or process known by the name of the inventor. He preferred in such cases, where the personal idea had been lost, to use no capital, but to write the name of the apparatus or process with a small letter, as, for instance, a gooch or an erlenmeyer. The same is true of materials or reagents with geographical adjectives, as for instance, german silver and canada balsam, both of which should be written with small letters, just as the French, without disparaging the great Emperor, write the name of the coin napoleon with a little n or as we write telford or macadam for the name of a road.

Chemists should be careful about "take." It is not elegant to say "take five grams and place in a dish." "Place five grams in a dish" is entirely sufficient. In one work on chemistry he found the author directing the analyst to "take twenty-five grams of Glauber salts" with a big g. "Weigh out" is inadmissable. We do not weigh out, nor in, nor on, nor under. We simply weigh. In measuring it is not necessary to say weigh, as the chemist knows enough to use the balance without specific directions. A typically unnecessary form of expression and one not impossible to find is "take barium chloride, weigh out five grams, dissolve in water and filter off the insoluble residue."

Above all, the scientific writer should avoid indulging in fine writing. Plain, unvarnished statement of fact in a clear, lucid manner is what we should strive for. An example of how not to write is the following:

"For not only does the soil make possible a very much greater profusion of land life than could otherwise exist, but it has also played an extremely important part in that long-continued never-ending, and sublime process of evolution whereby, as lands have insensibly changed into sea and seas into land, as mountains have risen so slowly and silently out of level plains as to spring their broad arches directly across wide rivers to the height of a

mile and yet leave their course unaltered, as climates have changed from cold to warm or from wet to dry, both plants and animals in this great drama of the world action have been enabled to change, not simply their costumes, but, if the exigencies of the new scene demanded it, legs for fins or even abandon them altogether and crawl upon their bellies through the grass."

Professor Bolton said he thought one's grammar school education must have something to do with style in writing. Great labor is expended nowadays upon abstracts from foreign publications. He thought there should be a different method of treating them. The results might be presented without giving the steps by which they are reached. He thought that no one could depend entirely upon the abstracts, but have to refer to the original papers for details.

Professor Seaman said he was glad the subject was brought up; he thought some chemists had an idea that the English language is sacred, and that no changes should be made in it. This feeling must be met. He said that most persons read by words, and not by letters, and if a word has not the usual appearance to which we are accustomed, our first impression is that it is wrong, and hence he feared that no changes, however judicious, would seem agreeable. As to the agreement of collective nouns with verbs, Goold Brown concluded that the only principle to be followed is euphony. When the best grammarians cannot formulate rules, uniformity can hardly be expected. As to the use of small letters instead of capitals, the various changes that are going on in the language generally ought to be considered. The councils of biological societies have agreed that small letters should be used. Up to a few years ago specific names derived from proper names were begun with capitals, but now the small letters are used. As to the abbreviations used for weights and measures, he said no system had universal assent. Physicists and mechanicians have in use a long series of abbreviations for linear, areal and cubic measures. In three of the most important German chemical works, including the "Berichte," small letters are used, for the liters (l); for the grams (g); and for cubic centimeters (cc.), and he would be in favor

of adopting these, but unfortunately the pharmacists and physicians who are endeavoring to introduce them into their arts, have agreed upon the capital G and small r for gram, and capital C and small c without a point between them for cubic centimeter. Remsen in his first edition used cc., g., and l. Which are chemists to follow? The French do not use habitually any abbreviations. Some chemists, unfortunately, have not adopted the new spelling.

Professor Clarke said that a friend who wished to become a journalist, had consulted a newspaper man, and the advice he received was simple—"Have something to say and say it." Sometimes the writer is not sure as to what he wishes to say, and he tries to say something else, and his writing becomes involved. Another fault which was observed, especially in those who have just returned from abroad, was that everything that has ever been written upon the subject is given in an article, and the discovery of the authors is either buried in the mass or occupies a very small place at the end of the article. He thought a logical order should be followed, and an effort should be made to state what is said, simply and clearly. He thought Steele's "Fourteen Weeks in Chemistry" was a model of bad style.

Professor Munroe said that so far in the discussion there was apparently very little difference of opinion. He read the following from an article in "Science." "If we hear a baby crying with two ears, are we to think it is twins?" as an example of style in a scientific article. He thought this illustrated Professor Clarke's remarks about having something to say and saying it. Professor Munroe thought that the question of style had to be considered from two standpoints: that of the manual or text-book, and that of the technical or scientific paper. Abbreviations that might be properly included in the latter, should not be introduced in the former until they have long been used in technical literature. He was especially doubtful as to the advisibility of changing the adjectives to the substantive as a "gooch, a bunsen, a ruhmkorff, or a wiley," and the latter suggests that where one is as fertile as our distinguished associate, there may be a difficulty in determining which one of his many devices shall be called a "wiley."

Dr. Fireman said he did not agree with what had been said as to abstracts. Many papers are not accessible, and possibly only one journal could be obtained. With a good abstract the description of a process may be of use. Neither did he agree with the idea that an historical sketch should be introduced. He thought a summary was frequently of greater use. They are generally brief and give valuable references.

Dr. de Schweinitz closed the discussion by saying that he agreed with Professor Munroe that the style should differ in text-books and in technical papers. What is proper in one is not so in the other. He thought that abbreviations should be dropped as the purpose is to make what is written useful to all, and he thought the ideas and the statements should be expressed as simply and clearly as possible.

A regular meeting was held Thursday, April 9, 1896, with the the President, Dr. E. A. de Schweinitz in the chair, and thirty members and ten guests present.

The minutes of the eighty-seventh meeting were read and approved.

A letter from Dr. Salmon, inclosing a circular letter from the Director of the Pasteur Institute in Paris was read, asking the society to appoint a member to represent it upon the committee to raise funds for the erection of a monument in Paris to Pasteur. The President, Dr. de Schweinitz, was unanimously elected to represent the Chemical Society upon this committee.

There being no further business the reading of papers was proceeded with.

The first paper of the evening was by Mr. V. K. Chestnut upon "Some Vegetable Skin Irritants and their Chemical Composition." The paper consisted of a review of the work of Dunstan and Miss Boole on Croton Oil, and of Pfaff on Toxicodendrol, a new oil-like body from the poison ivy, *Rhus radicans;* together with an account of some vesicating plants which have been but little studied. Specimens of this plant were exhibited and the effect of an alcoholic solution of lead acetate as an antidote to Rhus poisoning was illustrated by experiments carried

out by the writer on himself. These experiments also showed conclusively that toxicodendrol was the vesicating principle of the poisonous species of Rhus. Discussion was by Messrs. Tassin, Munroe, Cutter, Stewart, Fireman and de Schweinitz. Mr. Tassin asked whether it was the lead acetate or the alcohol that is the antidote. Mr. Chestnut answered that the alcoholic solution of lead acetate is the best remedial agent. If the oil is kept long enough on persons supposed not to be susceptible, they will be poisoned; the poisoning may take place at the end of twelve hours, or not for five days. Portions of the skin that are thick are not so easily affected as are those where it is thin. Professor Munroe gave his experience as to nitrobenzol, which he had used in considerable quantity, and to which he and the workmen were exposed; it was inhaled as vapor, and came in contact with the skin, but no one was poisoned. The vapor is suffocating, but the workmen soon became accustomed to it. All the books, however, state that it is poisonous. Mr. Cutter said that he could uphold the books, as he had experienced its poisonous effects; he had rigor, fever, chills, and palpitation of the heart, and was unconscious afterwards; the effects lasted for three days, and the smell even now would affect him. Dr. Stewart gave his opinion of its poisonous effects upon the skin; in his own case it had caused an eruption that lasted three or four hours. Dr. Fireman thought that different effects might be produced by vapors and by the liquid; he referred to the effect of hydrofluoric acid vapors, which are not poisonous in any degree, although the liquid was well known to be very poisonous. Professor Munroe thought there might be differences in the substance. Dr. de Schweinitz thought that possibly it was impure in the cases cited by Dr. Cutter and Mr. Stewart.

Mr. Ewell read the second paper of the evening on "The Effect of Acidity on the Development of the Nitrifying Organisms," by E. E. Ewell and H. W. Wiley.

"While it has been known for many years that active nitrification occurs only in the presence of some basic substance capable of neutralizing the free acid as fast as it can be formed, very little time has been devoted to the study of the exact degree of acidity that the nitrifying organisms can endure. As

the authors had some forty samples of soil at their disposal during the last year for other purposes, it seemed wise to improve the opportunity to test the influence of acidity on the nitrifying organism contained in the soils from various parts of the country. Tests were made with forty-four different soils, from twenty-two states and territories. The results showed great uniformity in the relation to acidity of the organisms contained in the various soils. Excluding five tests in which no nitrification exists, and five tests in which it was excessive because of the calcareous nature of the soils used for the seeding of the cultures, the average amount of nitrogen nitrified was twenty parts per million; the minimum result of the thirty-four tests included in this average was eleven, and the maximum twenty-five parts per million. The tests are to be repeated with pure cultures of the nitrifying organisms of the same soils. This series of experiments was made as a study of the nitrous organisms only, but the results show that the nitric organisms are not more sentitive to acidity than the nitrous organisms, the final product being nitrate in nearly every case.

Dr. de Schweinitz, referring to the action of acids on the growth of bacteria, said they seemed to be able to accommodate themselves to their environment, especially in the case of the tuberculous bacillus, and after a time they seemed to grow better in an acid medium than in any other, though at first they needed coaxing.

The third paper of the evening was on "The Chemistry of the Cactaceæ," by E. E. Ewell.

Until very recently other species of cacti than *Cereus grandiflorus* and a few related species have generally been regarded as devoid of constituents of pharmacological value. These and other species, have been used in medical practice in the countries in which they grow, but their use has rarely extended to the more civilized nations. Species of the genus *Anhalonium* have long been used for curative and ceremonial purposes by the Indians of Mexico, and the southwestern parts of our own country. They found places in the Mexican pharmacopœia of 1842, under the name of "pellote," or "Peyotl," but have been omitted from the later editions. The dried aerial portions of

species *Anhalonium* figure in the commerce of our southwestern border under the name "mescal buttons." The species of this genus have been the subject of scientific investigation by at least three groups of persons during recent years: First, a group of persons at Berlin, where the work was begun by Dr. L. Lewin, the crude material being supplied to him by Messrs. Parke, Davis & Co., of Detroit; second, a group of persons at the Pharmacological Institute at Leipsic, where the work has been conducted by Dr. Arthur Heffter; third, a group of persons in this country, centering in the Bureau of American Ethnology, and including as associates the Division of Chemistry of the United States Department of Agriculture for Chemical studies, Drs. Prentiss and Morgan for a study of physiological properties, and the Botanical Division of the United States Department of Agriculture for the settlement of botanical questions.

Lewin reported the presence of an alkaloid in *Anhalonium lewinii* in 1888. He has given this the name of anhalonin and made an extended report on its physical, chemical and physiological properties in December, 1894. He has also found evidence of physiologically active substances in the related species.

In August, 1894, Heffter reported the presence of a poisonous alkaloid in *A. fissuratum*, to which he gave the name anhalin; he found an extract of *A. prismaticum* to be physiologically active, but did not have sufficient material for a more extended study; he separated an alkaloid that he named pellotin from *A. williamsi*; in *A. lewinii* he found evidence of the presence of three alkaloids, the description of the first of which accords with the description of Lewin's anhalonin. He made an extended study of the chemical, physical and physiological properties of anhalin and pellotin.

In this country, the separation of the constituents of these plants, and the study of the action of the substances thus obtained as well as of the crude materials, upon men and the lower animals, were begun in the autumn of 1894, but before receiving the paper of Heffter. *A. lewinii*, in the form of "mescal buttons," has served as the material for these studies. Anhalonin and a second alkaloid have been separated in considerable quantity. These, as well as other constituents of the

drug, including one or more resins, are turned over to Drs. Prentiss and Morgan for physiological experiments, as rapidly as they are obtained in an appropriate state of purity. A complete chemical study of the constituents of the plant is in process, including those substances of interest to the vegetable physiologist as well as those of interest to the therapeutist.

The paper was illustrated with specimens of the cactus of different varieties from the Botanical Gardens and the Department of Agriculture. Mr. Mooney followed with a paper on "The Mescal Ceremony among the Indians."

The mescal plant is a small variety of cactus native to the lower Rio Grande Region, and about the Pecos River in Eastern New Mexico. The botanical name has finally been fixed by Professor Coulter as *Lophophora williamsi*. Mescal is the name by which it is known to the Indian traders, but it is not to be confounded with the other mescal (Maguey) of Arizona. The local Mexican name is *peyote*, a corruption of the original Aztec name, from which it would seem that the plant and ceremony were known as far south as the valley of Mexico, at a period antedating the Spanish conquest. Several closely related species are described by Lumholtz as being used with ceremonial rites among the tribes of the Sierra Madre.

The dry tops, when eaten, produce such marked stimulating and medicinal results and such wonderfully beautiful psychologic effects, without any injurious reaction, that the tribes of the region regard the plant as the vegetable incarnation of the deity, and eat it at regular intervals with solemn religious ceremony of song, prayer and ritual. The ceremonial and medicinal use of the plant was first brought to public notice by James Mooney in a lecture delivered before the Anthropological Society of Washington in 1891, as the result of studies made among the Kiowas and associated tribes of Western Oklahoma. As the ceremony is forbidden, and the trade in the plant made contraband upon the reservations, the investigation was a matter of some difficulty. In 1894 Mr. Mooney brought back a large quantity of the dried mescal, which was turned over to the chemists of the Agricultural Department for analysis, and to Drs. W. P. Prentiss and F. P. Morgan, of Washington, for

medical experimentation. The results thus far would seem to indicate that the Indians are right in asserting that they have discovered in the mescal a valuable medicine entirely unknown to science, and which will probably take its place in our pharmacopœia along with those other Indian remedies, quinine and coca. The ceremony and songs are briefly described by Dr. Mooney, whose full investigation of the subject will ultimately appear in one of the publications of the Bureau of American Ethnology.

Dr. Francis P. Morgan followed with a paper on the "Physiological Action and Medicinal Value of Anhalonium lewinii. ("Mescal Buttons.")" Dr. Morgan stated that the investigation had been intrusted to Dr. D. W. Prentiss, with whom he was associated. Experiments were tried and observations taken at regular intervals to determine the action of the entire button on the system. The most striking result was the production of visions of the most remarkable kind with eyes closed, and especially so in the dark. Changes of color were characteristic; tubes of shining light, figures, cubes, balls, faces, landscapes, dances and designs of changing colors were among the most persistent visions. They were hardly seen with the eyes open; in full dose no effect on the reason or will is noticed in most cases. There was direct stimulation of the centers of vision and dilatation of the pupils. About one-quarter of the quantity or three buttons, are sufficient to give the visions in the case of white men. Dr. Morgan detailed the experiences of different persons who had tried the experiments. In some cases there was slowing of the heart, from seventy-five to forty-five beats, followed by a rise to normal; there is also inability to sleep, and a loss of the sense of time—hours seem to intervene between words. The physiological action is not identical with that of any known drug, it is unlike cannabis indica, cocaine, etc. The constituents of the mescal buttons are being experimented with, but the investigations are still incomplete. Anhalonin causes increased reflex irritability and convulsions, like strychnine. It is evidently not the active principle; another constituent has been isolated whose action is widely different. It does not cause opisthotonos, nor tetanus, and has

no action like that of strychnine. A third principle has also been isolated. The resin is supposed to be the active principle and will probably be of use in medicine. The experiments are still being conducted and will be detailed later on.

Dr. de Schweinitz expressed the indebtedness of the Society to Mr. Mooney and to Dr. Morgan, and said that the further results would be of interest to the Society.

A regular meeting was held Thursday, May 14, 1896. The president, Dr. de Schweinitz in the chair, with twenty-three members present. Mr. Mayville W. Twitchell was elected as associate member and Mr. Charles N. Forrest as member. The president presented the following resolutions, endorsed by the executive committee, and the Society adopted them; the president and secretary were instructed to sign and transmit them.

WASHINGTON, D. C., May 14, 1896.

TO THE HONORABLE, THE PRESIDENT OF THE UNITED STATES SENATE.

DEAR SIR :—In view of the proposed legislation now before the Senate in the form of a bill entitled "An Act for the further prevention of cruelty to animals in the District of Columbia," which, however, is practically an act to limit, and eventually stop, all experiments upon animals in the District of Columbia, the Chemical Society of Washington, including among its members a number of the most prominent chemists in the country, desires to present to the Senate of the United States a formal and positive protest against the enactment of any legislation upon the subject of vivisection.

The laws at present on the Statute books of the District of Columbia, if properly carried out, will apply to all cases of cruelty to animals which exist in this District. The proposed bill is objectionable for very many reasons. The penalties prescribed for the infraction of the law are preposterous. An expert who did not happen to possess a permit from the District Commissioners for the performance of experiments upon animals might suddenly have placed in his hands material, the dangerous character of which could only be determined by an immediate experiment upon an animal. Should such a test be made without a license, though possibly the lives of hundreds of peo-

ple were involved, the experimenter would be subject to an enormous fine and imprisonment, for having in the interests of humanity inoculated a guinea pig, or a rabbit, or some other animal, without a formal permit from the District Commissioners.

While the majority of the members of our Society are not directly engaged in experiments in which animals are used, we know that in certain lines of work, toxicology, materia medica, biochemistry, and the like, animal experimentation is absolutely necessary for the advancement of knowledge.

The agitators of the proposed legislation have not been able to show a single instance of cruel experiments conducted in the District of Columbia, either in any of the laboratories, or medical colleges, or public schools, consequently there is no need for any law on the subject. Furthermore, Washington is becoming the center of education for the entire United States. Four large universities are located here; several more are in prospect, and the proposed legislation would hamper and eventually destroy all possibility for advanced postgraduate work in the biological science, and indirectly in all allied branches.

We therefore, collectively as a Society, and individually as members, desire to protest strenuously against any legislation on the subject of vivisection, deeming it to be unwise, unnecessary, and in direct opposition to the spirit which has for a number of years actuated the United States government to encourage the advance of science. We hold further that such legislation would be a direct contradiction of the well-known practical results that have already been obtained by scientific investigations conducted under the government, which have made possible the saving of many thousand dollars worth of property and many human lives.

Yours very respectfully,

[Signed] E. A. DE SCHWEINITZ,
Pres. Wash. Chem. Soc.

A. C. PEALE,
Secretary.

The president, representing the Society, as a member of the Pasteur Committee, reported that the committee had organized and was ready to receive subscriptions.

There being no further business the reading of papers was proceeded with, Vice President Bigelow taking the chair.

The first paper was by Mr. Frederick P. Dewey, on "Practical Analytical Accuracy."

The paper did not go into the means of securing accuracy, but dealt entirely with the results actually obtained when a number of chemists worked upon the same sample. Not very much has been published in this line, but sufficient has been done to show that the ordinary accuracy of analytical work is not what it ought to be and that there is room for much improvement.

The paper gave results from analytical symposiums published in the Transactions of the American Institute of Mining Engineers and the Proceedings of the Association of Official Agricultural Chemists. It was also somewhat historical in character in tracing the development of accuracy in some determinations.

The discussion of Mr. Dewey's paper was by Messrs. Bigelow and Clarke.

Mr. Bigelow said that Mr. Dewey had selected the most accurate of the determinations by the Official Agricultural Chemists, but Dr. Dewey said he had simply taken those most nearly in his own line of work. He referred to Campbell's tables in the Journal and thought it was unfortunate that nothing was said as to the way they were obtained nor how he was led to adopt the various figures. He allows usually a small variation, but with silica he allows a variation of over one-half per cent, when large quantities are present.

Prof. Clarke thought that a great source of variation between different observers was due to the fact that too great faith was placed in the reagents. The work was not done with the same reagents and reagents are not always the same. Here, therefore, is a source of error.

Mr. Bigelow said he thought another source of error was due to the fact that the work was often done by students or subordinates and these results were published with the others.

Mr. Dewey said his paper was intended to exhibit what was actually obtained every day. He thought the assistant's work was not always the poorest. The principal very often was out of practice.

Dr. P. Fireman read a paper on "A New Mode of Formation of Tertiary and Quarternary Phosphines." When phosphoni-

um iodide is heated with ether in a sealed tube at 160°, for si hours, both ethyl groups of the ether became available for sub stitution, and these form the hydriodic salts of triethyl- an tetraethylphosphine according to these equations :

$$2PH_4I + 3(C_2H_5)_2O = 2P(C_2H_5)_3.HI + 3H_2O.$$

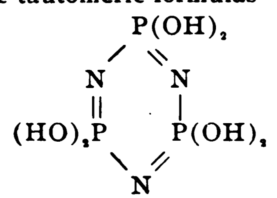
$$2PH_4I + 4(C_2H_5)_2O = 2P(C_2H_5)_4I + 4H_2O.$$

The author is at present occupied with the preparation of th homologous phosphines by the action of PH_4I and homologou ethers. He is also experimenting with a view of obtainin amines by the action of ammonium iodide or ammonium bromid on ethers or alcohols.

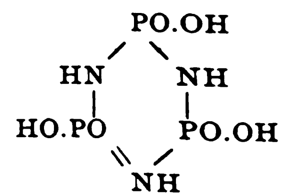
In the discussion of Dr. Fireman's paper Dr. Stokes asked i he had obtained any traces of primary or secondary phosphines Dr. Fireman answered that primary phosphines are exclude and as to secondary phosphines he had at one time hoped h had obtained them, but he could not say with any certainty tha he had. Dr. Stokes thought they might be recognized by the odor. Tertiary phosphines have the odor of hyacinths.

Dr. Stokes then read a paper on "Metaphosphinic Acids."

Dr. H. N. Stokes spoke on his investigation of the metaphosphinic acids, a series of acids having the general formula $(PNO_2H_2)_n$, *i. e.*, metaphosphoric acids in which one-third of the oxygen is replaced by NH. They are not, however, strictly speaking, derivatives of metaphosphoric acids, for while these contain a nucleus consisting of phosphorus atoms united by oxygen, the metaphosphinic acids, as proved by their formation from the chloronitrides $(PNCl_2)_n$, have a nucleus consisting of alternate phosphorus and nitrogen atoms. Two members of the series have been studied, *viz.*, trimetaphosphinic and tetrametaphosphinic acids, $P_3N_3O_6H_6$ and $P_4N_4O_8H_8$, derived from $P_3N_3Cl_6$ and $P_4N_4Cl_8$. Trimetaphosphinic acid apparently has the tautomeric formulas



and



Salts of both forms have been obtained. Under the action of acids, a successive decomposition is effected into $P_3N_2O_8H_7$, $P_2NO_6H_5$, $H_4P_2O_7$, and H_3PO_4. The second of these may be regarded either as $PO(OH)_2.NH.PO(OH)_2$ or $PO(OH)_2.O.PO<^{NH_2}_{OH}$, the former being supported by its derivation from $P_3N_3O_6H_6$, the latter by its easy conversion into pyrophosphoric acid. It presents a peculiar case of intra-molecular wandering of the nitrogen atom, possibly to be explained by a process analogous to Beckmann's transformation. (Particulars will appear in the American Chemical Journal.)

Dr. Fireman said the compounds appeared to him to be of similar constitution as cyanic acid and its derivatives; and also in regard to the tendency to polymerize and to appear in isomeric forms, there is a striking resemblance between both classes of compounds. He thought the results would be of interest in theoretical chemistry. As to the silver salts he asked Dr. Stokes if he had tried to prepare the esters.

Dr. Stokes said that a number of lactams are known that are stable, that open out or have open rings in which the tendency to break up is not marked. The tri acid is easily broken up but the tetra acid is not. In regard to the esters, he had tried to get them from the silver salts, but they are not like the organic ethers. They are very unpleasant to deal with and are coupled mixtures with which little can be done. He had thought of the analogy with cyanic acid and especially with the cyanuric acid compounds. Another theoretical point is the possibility of stereo-isomeric forms. When you have an oxime there are two isomers known. They split up differently — cis and trans bodies. He had not been able to find triphosphinic acid in any but two tautomeric forms.

Prof. Munroe said he was glad to see that the methods of organic chemistry were being applied to inorganic chemistry, but he would like to know why the linear form of the salts was written one way, and read in the reverse way in organic chemistry. He thought it was very confusing to students.

Dr. Stokes thought it was a matter of custom.

Dr. Fireman said he thought that the reason for writing the formula of the organic acid first and then that of the metal was due to the fact that the formulas of the organic acids were usually of a complicated nature and therefore it is natural to dispose of them first and that afterwards it is an easy task to fit in the symbol of the metal.

Prof. Munroe thought this was not the explanation.

Dr. Stokes said different men developed the two methods working from two different sides when a series of homologous compounds is written out. The constants are put down first and then those that vary. This was why he wrote them this way.

Prof. Seaman thought this the correct explanation. Ideas have a different arrangement with different people, normal to each one. He thought there was more uniformity in this country than anywhere else.

The Society adjourned until November.

Issued with July Number, 1896.

Proceedings.

NEW MEMBERS ELECTED JUNE 25, 1896.

Hanna, Prof. Geo. P., Charlotte, N. C.
Harsh, S. A., Revenue Gold Mining & Milling Co., Norris, Mont.
Lederle, Ernest Joseph, Ph.D., Health Department, N. Y. City.
Ludwig, H. T. J., Mount Pleasant, N. C.
McFetridge. Joseph, Natrona, Pa.
Melville, W., Woodmere, Mich.
Mewborne, R. G., Raleigh, N. C.
Miller, H. K., Raleigh, N. C.
Parmelee, Cullen W., 108 Tenth St., Greenpoint, Long Island.
Pegram, W. H., Durham, N. C.
Smalley, Frank W., University of Cincinnati, Cincinnati, O.
Thompson, F., 102 East Seventh St., Covington, Ky.
Uhlig, E. C., care of Whitall, Tatum & Co., 46–48 Barclay St., N. Y. City.
Wood, Joseph R., 240 Green Ave., Brooklyn, N. Y.

ASSOCIATES ELECTED JUNE 25, 1896.

Howell, John W., Edison Lamp Works, Newark, N. J.
Twining, T. E., Newark, Ohio.

CHANGES OF ADDRESS.

Behr, Arno, P. O. Box I, Jersey City.
Eakins, L. G., Box 434, Florence, Colo.
Lane, H. M., care of Great Falls Iron Works, Great Falls, Mont.
Lenher, V., Mechanicsburg, Pa.
Peter, Alfred M., 236 East Maxwell St., Lexington, Ky.
Sargent, Geo. W., Bellwood, Blair Co., Pa.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The regular meeting of the Section was held Saturday evening, May 16th.

Dr. S. P. Kramer presented "Some New Facts Concerning X Rays," giving an interesting account of some experiments, and

exhibiting some negatives made by means of his new five plate Töpler-Holtz machine.

Mr. B. M. Pilhashy, of Cincinnati and Mr. J. N. Hurty, of Indianapolis, were elected members of the Section.

The meeting adjourned until October 15th.

NEBRASKA SECTION.

The Nebraska Section held its fourth regular meeting on June 5th, at 8:00 P. M.

The meeting was called to order by the president. In the absence of the secretary, Mr. J. B. Becher was elected Secretary *pro tem.*

The minutes of the last meeting were read and adopted.

The following officers were elected for the ensuing year: President, H. H. Nicholson; Secretary aud Treasurer, Dr. John White; Executive Committee, Samuel Avery, R. S. Hiltner and J. F. Becher.

The Secretary's report was read and approved.

The Treasurer's report having been read, Mr. E. C. Elliott and Miss Rosa Bouton were appointed an auditing committee.

The committee pronounced the report correct, whereupon it was approved.

A letter from J. Stanley Brown, Secretary of the Joint Commission of the Scientific Societies of Washington, was then read, calling attention to the anti-vivisection bill now pending before Congress.

The President appointed a committee to draft suitable resolutions, which were adopted.

"WHEREAS, There is now pending before the Congress of the United States a bill entitled 'A bill for the further prevention of cruelty to animals in the District of Columbia;' and

WHEREAS, In our opinion such legislation is opposed to the proper development of biological and medical science; and

WHEREAS, It is feared that such legislation may be further extended to the several states and territories, thereby very seriously restricting the progress of scientific investigation; be it

Resolved, That the Nebraska Section of the American Chemical Society most earnestly protests against the enactment of such

legislation as being unnecessary and prejudicial to the best interests of mankind.

Signed,

H. H. NICHOLSON, President.
ROSA BOUTON,
JOHN WHITE,
EDWARD ELLIOTT,
Committee.

Mr. Benton Dales was elected an associate member.

In the absence of Dr. White, his paper entitled "Contributions to the Chemistry of the Suboxides," was read by Mr. E. E. Nicholson.

NEW YORK SECTION.

The June meeting of the New York Section was held on Friday evening, June 5th, at the College of the City of New York, Prof. A. A. Breneman presiding.

After the reading of the minutes the chairman of the committee on Organization of the Chemical Club reported that at a recent meeting of the committee, held at the Board of Trade, much enthusiasm was shown, and the movement was making good progress.

A communication from the Joint Commission of the Scientific Societies of Washington in regard to the Senate bill 1552, intended to restrict, if not prohibit, vivisection, was taken up and acted upon.

The sentiment of the meeting was unanimous in the direction of preventing affirmative action by Congress on the said bill; and the following resolutions were unanimously adopted, after a full discussion, in which Profs. Sabin, Breneman, Doremus, Hale, and McMurtrie participated.

Resolved, That the New York Section of the American Chemical Society most earnestly opposes the legislation proposed by Senate bill 1552, entitled "A bill for the further prevention of cruelty to animals in the District of Columbia."

Resolved, That the proposed legislation is unnecessary and would seriously interfere with the advancement of biological science in that district; that it would be especially harmful in its restriction of experiments relating to the cause, prevention, and cure of the infectious diseases of man and of the lower animals; that the researches made in this department of biological

and medical science have been of immense benefit to the human race; and that, in general, our knowledge of physiology, of toxicology, and of pathology, forming the basis of scientific medicine, has been largely obtained by experiments upon living animals, and could have been obtained in no other way.

Resolved, That physicians and others who are engaged in research work having for its object the extension of human knowledge and the prevention and cure of disease are the best judges of the character of the experiments required and of the necessity of using anesthetics, and that in our judgment they may be trusted to conduct such experiments in a humane manner, and to give anesthetics when required to prevent pain. To subject them to penalties and to espionage, as is proposed by the bill under consideration, would, we think, be an unjust and unmerited reflection upon a class of men who are entitled to our highest consideration.

Dr. C. A. Doremus read a "Note on the Presence of Oil in Boiler Scale."

Mr. J. A. Matthews described "A New Method of Preparing Phthalimide."

The chair announced this as the last meeting of the season, and stated that the fall and winter meetings would probably be held in the same rooms.

Issued with August Number, 1896.

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COUNCIL.

Dr. Drown having resigned from the Committee "to unify the methods of color comparison and report on a standard for measurement of color in potable waters," the President of the American Chemical Society has appointed in his place Mr. Allen Hazen, 85 Water St., Boston, Mass. and Mr. Hazen has accepted the appointment.

CHANGES OF ADDRESS.

Bloomfield, L. M., Ohio Experiment Station, Wooster, Ohio.
Booraem, J. V. V., Box 190, Glen Cove, N. Y.
Fuller, Fred. D., Durham, N. H.
Lippincott, Warren B., North Western Iron Co., Mayville, Wis.
Mar, F. W., 138 First Ave., West Haven, Conn.
Myers, H. Ely, Carnegie Steel Co. Ltd., Lucy Furnace, Pittsburg, Pa.

MEETINGS OF THE SECTIONS.

NORTH CAROLINA SECTION.

The summer meeting was called to order at 3.30 P. M., July 7th, in the Chemical Lecture Room of the University of North Carolina. There were ten members in attendance. The secretary reported ten new applicants for membership, who were duly elected. There were other applicants who had not yet conformed to the condition of becoming members of the American Chemical Society. The membership roll has doubled in less than a half-year.

Resolutions were offered and adopted with regard to the vivisection bill and the appointment of a director-in-chief of the Scientific Bureaus of the Department of Agriculture. The following papers were then read:

"Crystallized Aluminum," by F. P. Venable; "Detection and Purification of Saccharin," by B. W. Kilgore; "Reduction

of Sulphuric Acid," by Chas. Baskerville; "Comparison of Digestibility of Raw and Steamed Cotton Seed," by J. A. Bizzell; "An Attempt to Form some Organic Compounds of Zirconium," by Thomas Clarke; "Determination of Sulphur in the Presence of Iron," by W. A. Withers and R. G. Mewborne; "Action of Phosphorus Trichloride on an Ethereal Solution of Hydrogen Dioxide," by W. A. Withers and G. S. Fraps; "Some Difficulties in the Way of the Periodic Law," by F. P. Venable.

The section then adjourned.

Issued with September Number, 1896.

Proceedings.

CHANGES OF ADDRESS.

Beeson, J. L., Bethel College, Russellville, Ky.
Best, Dr. Otto, care of Fritzche Bros., Garfield, N. J.
Haines, Reuben, Haines and Chew streets, Germantown, Pa.
Emmens, Stephen H., 179 Washington Building, N. Y. City.
Kelley, J. H., Bentonville, Ark.
Moale, Philip R., 82 Chestnut street, Asheville, N. C.
Mumper, W. N., 823 W. State street, Trenton, N. J.
Nichols, Wm. H., 32 Liberty street, N. Y. City.
Potter, Wm. R., 100 Broad street, Providence, R. I.

DECEASED.

Bower, Henry, Gray's Ferry Road, Philadelphia, Pa.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The regular monthly meeting of the Rhode Island Section was held at Providence, May 21, 1896, Mr. Charles S. Bush in the chair.

A paper was presented by Mr. William R. Potter, upon "Fallacies in Urine Analysis due to the Presence of Salicylic Acid and its Compounds."

After a brief introduction of the value of urine examination as an aid to the physician in his diagnosis, the reader described in detail the influence salicylic acid had upon the albumin test and the glucose test as commonly practiced. The chief source of error was pointed out to lie in the sparing solubility of salicylic acid in an aqueous solution, and the ease with which its compounds were decomposed by other acids.

The annual meeting of the Rhode Island Section was held at Pawtucket, R. I., on Thursday afternoon, June 11, 1896.

Members met upon the invitation of the presiding officer, Mr. C. A. Catlin, at the Country Club. After dinner the annual election of officers took place. The following were elected for the ensuing year:

Presiding Officer, Mr. Edward D. Pearce ; Secretary and

Treasurer, Mr. Walter M. Saunders; Member of the Executive Committee, Mr. George F. Andrews.

The retiring chairman then presented his annual address, taking for his topic, the subject of chemically-applied mechanics, introducing it by brief historical reference to the progress of chemistry, more particularly to the development of apparatus and improvements along the line of chemical manipulation. It appears that after all the same forms of retort and crucible that did service in the time of Zosimus, are still the stereotyped forms of the chemical supply house.

Great progress in recent years in arts dependent upon chemistry, has, however forced the development of apparatus, and the application of mechanical expedients, until there has grown up what may in all truth be called the science of chemically-applied mechanics, practically unrecognized as yet by the training schools of the profession, though covered in a general way by courses offered in chemical engineering. These courses do not meet the case. The real demand is, that chemical students shall have opportunity in training, to pursue the study of practical mechanics as applied to chemical manipulation, simply a new study added to the old curriculum. Illustrating something of the scope of this chemically-applied mechanics, may be cited, hydraulics, for instance, as applied to the handling of liquids, the speaker showing from his own practical experience how the attendant phenomena of the various filtering methods, may, by a general classification, be brought to useful presentation of the whole subject. Further may be cited pneumatics as applied to the manipulation of air draughts, the charging of liquids with gases, etc., strength and adaptability of materials to the construction of apparatus, their acid or alkaline resisting qualities, with effects of saline solutions upon them; heat in its varied application; light in the practical application of its actinic properties; and the milling of materials. Again illustrating particularly, the speaker showed how the attendant phenomena of the various milling processes may be brought under general statements for better consideration.

Generally the scope of chemically-applied mechanics may be stated as the application of mechanical principles to chemical manipulations. The whole subject should be presented to the chemical student in a general way, setting forth at least the fundamentals along these and related lines, expanding into particular detail in the more important, thus broadly laying the foundation for the development and exercise of the inventive faculty in applying mechanical means to special chemical requirements, whether it be in the factory or the research laboratory.

Issued with October Number, 1896.

Proceedings.

THIRTEENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

BUFFALO, N. Y., August 21, 1896.

President Dr. Charles B. Dudley called the meeting to order. Dr. Roswell Park, President of the Buffalo Society of Natural Sciences, welcomed the visiting chemists as follows:

Mr. President and Gentlemen of the Chemical Society: I am very glad to join with my friends in the City of Buffalo in welcoming you here. My idea of what should be said on such an occasion, is that it should be characterized by genuineness rather than eloquence, by brevity rather than length. I am sure we are very glad to see you here. I know that this is the first time the Chemical Society ever met in Buffalo, and we hope that you will like us so well that you will come again. I have on several occasions in time past welcomed associations of citizens here. I tell them we have pleasant weather here always. I was sure in my own mind that you would have it. It is a promise we can safely make anytime in the summer. Buffalo seems to be generally regarded now as the ideal convention city. We have had a convention here of some kind almost every week, and this will continue through September. There are meetings here almost all the time. If you study our statistics you will find us the healthiest city in the country. If you will travel around our streets you will discover we have the most attractive residential city in the country. And in every way, both from our treatment of you and what you see for yourselves, we hope you will feel thoroughly welcome, and thoroughly at home.

It is always proper, I think, on such occasions, to blow our own horn a little bit. I have found so little appreciation of Buffalo abroad, of what Buffalo is, that I am going to say a little to you about Buffalo. It is the sixth commercial city in the world. That is not generally appreciated. A friend of mine went to Boston and while there was talking to a friend of his in that city about Buffalo. The Boston man said, "Buffalo? Is that on Lake Erie or Lake Ontario?" At the same time, we have a much greater tonnage coming into our harbor in one year than comes into Boston harbor. That he overlooked. About 5,000,000 tons of tonnage enter our harbor, and about the same leave our harbor every year. There is only one other city can say this, and that is Liverpool. That is not generally appreciated. Thirteen years ago, when I moved here, the city had about 125,000 inhabitants; now it has a third of a million, so

you can get an idea of how it is growing. We who live here and see th trend of affairs, look forward to a time when there will be but one city t Niagara Falls. We are coming nearer and nearer to that all the time It is not far off, I assure you.

Now, with all we have and all we can do for you, gentlemen, you ce tainly are cordially welcome. You will hear more of this, as I expec you will attend the meetings next week, and perhaps be more formall welcomed by the city officials on other occasions; but our homes ar opened to you, and everything we can do in any way for you, is cordiall placed before you.

To refer just a moment to the scientific aspect of this gathering, I hav never had a chance to talk to professional chemists before, and there i one appeal I want to make to you as coming from our profession to yours Of course we are working in large measure on common ground; espe cially when it comes to physiological chemistry, and in the chemistry o the fluids, etc., of the body, we are on absolutely common ground; bu there is very much we have to rely upon you for, in order to help our selves forward; and, as one who is eagerly anxious for the discovery of a particular substance, an ideal in our business, which you only can prob ably furnish, I will make this scientific appeal to you. We have been working for years to find a substance which shall have a germicidal prop erty so far as deleterious agents are concerned, and yet which will not be toxic with the tissues of the human body; a chemical substance whose relative and absolute toxicity are far enough apart to make it a safe sub stance to use. When we have that, we hope to saturate the human body with the substance which will be at the same time not toxic with the tis sues of the larger organs. I do not know whether that time will ever come. It seems to me an ideal substance. I do not know how you, who are so interested in the affairs of the world at large, as well as humani tarians, can make a better discovery than one along the lines I have sug gested. It is not for commercial purposes, but purely for the benefit of humanity. You will pardon this little appeal to your chemical abilities; it is the only chance I have ever had to make it.

Permit me only to reiterate what I have said to you about the cordial ity of our welcome, our earnest endeavor to extend to you our hospitality, our earnest hope that your first meeting will not only be so successful that you will look back to it hereafter, but will be so pleasant to you that you will want to come here again quite often. (Applause.)

The President.

Dr. Park, The Committee of Arrangements, and Fellow Members of the American Chemical Society: I am sure I voice the sentiment of those who are present when I say that we appreciate this kind welcome, and we thank you for it. I doubt not there are a good many present who can well remember when chemical analysis, except for purely scientific pur-

poses, was a rarity. In my early student days the chemical analyses that were made, except as I say, for such purely scientific purposes, were largely made by the professors in colleges. They were slow. They were very expensive and any business that wanted a chemical analysis, studied quite a while before employing a chemist to make it. That state of affairs is now changed. With the growth of the technical school there has come forward each year a large crop of young, enthusiastic chemists, and with this supply, if I may use the word, has come likewise the necessity for their existence and the work for them. I am not saying anything more than is known to you all when I say that a very large number of commercial ventures and enterprises to-day cannot live without their chemist. The steel works would not be able to maintain themselves a month without a chemist. The sugar industry needs the chemist, the brewing industry, the textile industry, and, indeed, I might go on and enumerate occupation after occupation which is based largely upon the chemist's work. The railroads, as you know, are using chemists, and the cities begin to have their chemists to protect people against fraud and adulteration in products which are for sale. As we all know, agriculture is more and more every day becoming based on chemistry, and our government itself supports one of the best chemical establishments in the world.

Now, this increase in chemists, this increase in their work, this demand for them, has led to another necessity; namely, that the chemists should occasionally look each other in the face, that they should talk things over with each other, that they should profit by each other's work, and that brings us to state what the organization of the Chemical Society is, an organization with something like 1,000 members, an organization which supports a Journal that is published every month, and with some eight or nine local sections located in different parts of the country. This organization must, as we all know, have a place for meetings. We are already having two meetings every year and this year we come to Buffalo, and I may say, that this city is the Mecca to which all scientific men are travelling this year—this city which may almost be called the mother of scientific organizations. I believe that the reorganization of the American Association for the Advancement of Science, one of the oldest scientific organizations in the country as we all know, took place here in Buffalo in 1866, after the war. It had previously had existence but the war injured it, or caused a temporary cessation and the reorganization took place in Buffalo. Thus much for our reason for existence and thus much for our coming here. We appreciate very greatly your kind and gracious welcome. We look forward to an interesting and profitable time. We thank you. (Applause.)

The following papers were then read and discussed:

"Mercuric Chlorothiocyanate," by Charles H. Herty and J. G. Smith. Read by Dr. Herty. Discussed by Messrs. Hart, Prescott and Frankforter.

"The Reduction of Concentrated Sulphuric Acid by Copper," by Charles Baskerville. Read by the author.

"Notes on the Preparation of Glucinum," by Edward Hart. (An informal description of the progress of work on the preparation of glucinum and its alloys. A glucina crucible was exhibited and also some nearly pure glucina prepared by the method already described in the Journal, **17**, 604. This glucina apparently contains the same unknown substance already detected by Kruss, and as 200 pounds of beryl are being operated on it is hoped that enough may be obtained for its identification.) The paper was discussed by Messrs C. B. Dudley and Hart.

"The Inspection and Sanitary Analysis of Ice," by C. L. Kennicott. Read by the author. Discussed by Messrs. W. P. Mason, Cochran, McKenna, W. A. Noyes, Breneman, Miller, Phillips, Robbins, Frankforter and C. B. Dudley.

"A New Form of Potash Bulb," by M. Gomberg. Read by Dr. Prescott. Discussed by Mr. Phillips.

"Morphine in Putrefactive Tissue," by H. T. Smith. Read by Dr. Prescott. Discussed by Mr. Miller.

"Some New Compounds of Thallium," by L. M. Dennis and Martha Doan, with crystallographic notes by A. C. Gill. Read by Dr. Dennis. Discussed by Messrs. Prescott, Hart, Frankforter and Mason.

The President: It has reached pretty nearly the hour of adjournment and I would like to make an announcement or two as to the work of the Society during the interim. Early in the spring a letter was received by the Society stating that Cannizzaro's seventieth birthday was to occur on the 11th of July, and it was proposed to make a testimonial to him in some way. This letter asked the cooperation of the American Chemical Society. After talking the matter over it was decided since Cannizzaro was already an honorary member that we should send him a testimonial engrossed on parchment. This was duly prepared and was sent in time to reach Rome some two or three weeks before his birthday. However, since that time we have received a second letter stating that owing to the fact that most of the professional people who were interested in Cannizzaro were out of town during the very warm season, it has been decided to postpone the public recognition of the occasion until later in the fall, I think some time in October. So we have not as yet heard

from the other side as to what has been done with the testimonial. I would say likewise that in this letter there was a statement to the effect that the form, which recognition was taking on the other side was that of accumulating a fund to be used for some scientific purpose.

I would also state that at the last meeting of the Society in Cleveland a committee of three was appointed to take up the question of coal analysis. That committee consisted of Mr. Hillebrand of the Coast Survey, Chairman, Prof. W. A. Noyes and the President of the Society. The committee has been able to do very little thus far except to get ready. They are not prepared to make any formal report at this meeting, partly, I think due to my own fault in the matter. Our progress has not been sufficient to make a formal report. This is simply to let you know that the subject has not been dropped.

About the beginning of the summer a paper was read in the New York Section by Prof. Leeds on the color of water, and at his suggestion a Committee was appointed to report to the Society, a standard to be used for determining the color of water and a method. That committee consists of Prof. Leeds, Chairman, Prof. Mason and Mr. Allen Hazen, formerly connected with the State Board of Health of Massachusetts, who has done a good deal of work on water analysis. We have some regular or standing committees; I have not been able to get in communication with the Chairmen of all of them as yet, and we will try to-morrow to see whether we can get information from them on the state of the subjects committed to them. After some announcements by the general secretary and the local committee of arrangements, the session adjourned.

SATURDAY MORNING, AUGUST 22, 1896.

The President called the Convention to order at 9:40 o'clock.

The President: As we have considerable to get through with to-day I think we had better start as soon as possible and first of all I will ask the Society to give two or three minutes to Dr. de Schweinitz who wants to present the matter of the Pasteur monument.

Dr. de Schweinitz: Mr. President and gentlemen of the

Society : I only desire to detain you for a moment to ask for subscriptions towards the erection of an international monument in Paris to Pasteur. The French Government has organized this movement and requested the cooperation of all scientists, or I should say, rather, of all members of the different branches of science in the United States. As Pasteur was a chemist, the chemists of the United States should be the first to respond to this request. Printed blanks of a general announcement, giving the names of the members of the French committee, and also of the organizing committee of Washington, which has been started, will be distributed, and in addition to this subscription blanks, as you see here, upon which you are requested to place the amount, however small, it does not make any difference, and however large, the larger the better and the more will the contribution be appreciated, to be forwarded to Washington. These blanks with the names and the amounts will be preserved and will be deposited in Paris in the archives in connection with this Pasteur monument. I will distribute these blanks and be greatly obliged to the members of this Society if they will join in the contribution at as early a date as possible and to the largest amount that they feel able to give.

The President : I am sure the appeal is one that we are all interested in, and if chemists can see their way to subscribe for this purpose, we shall be very glad. We all feel willing undoubtedly, but possibly not all of us are able.

Dr. de Schweinitz : Mr. President, I might add that the subscriptions so far received have varied in amount from twenty-five cents up, so that no one need have any hesitancy on that subject.

The President : I presume there is no one can not subscribe at least the minimum amount.

I wish to say that Dr. Levi has brought up a few samples of aniline colors made at the aniline works, which there was no opportunity to distribute yesterday, and anyone here can avail himself of the samples if he so desires.

The following papers were then read and discussed :

"Contribution to the Knowledge of Rutheno Cyanides," by James Lewis Howe. Read by the author.

"Analytical Methods Involving the Use of Hydrogen Dioxide," by B. B. Ross. Read by the author.

Prof. Hart: Mr. Chairman, while we are waiting for Prof. Ross to place these figures on the blackboard, there is a matter that has been called to my attention which I would like to present to you; it will only take a half minute; this is connected with the subject of advertising for the Journal. By resolution of the Board of Directors I was appointed a committee of one to secure advertisements for the Journal. This is an important source of revenue, and we have derived considerable money to be applied to the publication of the Journal in this way. It is believed that with some additional assistance this source of revenue can be still further increased. We have to depend for this assistance on voluntary aid, and I wish to acknowledge the great assistance I have already received from Dr. McMurtrie in this direction. The Society is indebted to him more than is perhaps generally known. It has been suggested to me that a number of members of the Society would be willing to assist in the matter of procuring advertisements, and that it would be well to increase the committee to ten members. These members would then feel that it was their duty to assist in securing the advertisements, and it is believed that this will result in securing considerable additional patronage. I therefore move that the President have power to increase the committee to not more than ten members.

Dr. Hale: I second the motion.

Dr. McMurtrie: I think it might be well further to give the committee power to extend its membership in case that appears desirable. I would move to amend in that manner.

Prof. Hart: I accept the amendment.

President Dudley put the motion as amended, and it was duly carried.

The following papers were then read:

"The Estimation of Thoria; Chemical Analysis of Monazite Sand," by Charles Glaser. Read by Dr. Hart.

"The Estimation of Thorium and its Separation from Other Rare Earths," by L. M. Dennis. Read by the author. These two papers were discussed by F. W. Clarke and L. M. Dennis.

"A Complete Analysis of Phytolacca Decandra," by G. B. Frankforter and Francis Ramaley Read by Mr. Frankforter.

"The Crystallized Salts of Phytolacca Decandra," by G. B. Frankforter and Francis Ramaley. Read by Mr. Frankforter. Discussed by A. B. Prescott.

"The By-Products formed in the Conversion of Narcoline into Narceine," by G. B. Frankforter. Read by the author.

"The Composition of American Kaolins," by C. F. Mabery and Otis T. Klooz. Read by Dr. Hart. Discussed by Messrs. Dudley, Baskerville, McMurtrie, Noyes, Prochazka, Breneman and Patrick.

The following papers were read by title:

"Composition of Certain Mineral Waters in Northwestern Pennsylvania," by A. E. Robinson and Charles F. Mabery.

"Zirconium Oxalates," by F. P. Venable and Charles Baskerville.

"Aluminum Analysis," by James Otis Handy.

"An Analytical Investigation of the Hydrolysis of Starch by Acids," by George W. Rolfe and George Defren.

"The Effect of an Excess of Reagent in the Precipitation of Barium Sulphate," by C. W. Foulk. Discussion by T. M. Gladding.

"Determination of Reducing Sugars in Terms of Cupric Oxide," by George Defren.

"Acidity of Milk Increased by Boracic Acid," by E. H. Farrington.

"The Actual Accuracy of Chemical Analysis," by Frederic P. Dewey.

"Some Extensions of the Plaster of Paris Method in Blowpipe Analysis," by W. W. Andrews.

"Device for Rapidly Measuring and Discharging a Definite Amount of Liquid," by Edward L. Smith.

"Table of Factors," by E. H. Miller.

"A Modified Form of the Ebullioscope," by H. W. Wiley.

"The Signification of Soil Analysis," by H. W. Wiley.

"Notes on the Determination of Phosphorus in Steel and Cast Iron," by George Auchy.

"The Development of Smokeless Powder," by C. E. Munroe.

The President: I would like to announce that the winter meeting will be held in Troy, it having been decided by the Council,

on the invitation of our membership in Troy to hold the meeting at that place. We are hoping to make that meeting one of the best the Society has ever had and I would like to ask Prof. Mason to give us a word or two in regard to our meeting next winter at Troy.

Prof. Mason : Mr. President and fellow members, it has been very gratifying to me to learn that you have decided to come to Troy. We are not a large city, but we will do our very best to make your stay agreeable. There are some things there that are worth seeing. We will be able to show you the largest gun plant in the world, much larger than Krupp's. Of course when you speak about Krupp's plant it means his whole concern, the gun plant and that for other varieties of iron and steel manufacture as well, but the gun portion of his plant would go into a small part of the United States gun plant which you will see at Troy. As you know, all the artillery now used by the army is made there, practically ; I believe there are a few unfinished contracts out, but I am not positive about that. You will be able to see electric cranes that I think are larger than you have ever seen elsewhere. You will be able to see guns in all stages of manufacture. I hope you will be able to see an old-fashioned smooth bore of fifteen or twenty inches caliber lying along side of a modern twelve or thirteen. It looks like a soda water bottle. We have some other institutions there that we are proud of, for instance the new basic steel plant, which will be in full operation by the time you get there, the Burden Iron Works where they make Burden's best iron, which you have often heard of. The shirt foundries and collar smelting works with their attendants are well worth seeing. (Laughter.) More particularly the E & W Collar. You have probably heard of them. They have sent you a special invitation. We have $N+1$ breweries in Troy. We can take care of the N and we have assigned the 1 to our President. (Laughter.)

It will give us great pleasure to see you and I am heartily glad that you are coming and the Mayor of the city sends his especial invitation.

The President : I am sure we will all look forward to this

meeting with a great deal of interest, and as I said at the very outset we hope to make this the most important meeting the Society has ever had. At this point and *a propos* here I want to give you a word of exhortation in regard to the condition of the society. As everybody knows the most important thing in the Society is the Journal. The Journal is impossible without money. Our rates are low, our annual dues being only \$5.00. The Society of Civil Engineers in this country charges \$15.00, the Mechanical Engineers \$15.00, the Mining Engineers \$10.00, the Mining Institute of Great Britain two guineas ; the German Mining and Steel Institute charges \$10.00. We are trying to run a Society on \$5.00 and the management does not think at present that it would be advisable to raise that figure. But we want more money. How can we get more money ? Obviously by getting more members. If every member of the Society would get one, think what would happen the doubling of our membership. It is believed there are something like 5,000 chemists in the United States who are eligible, either as full members or associates. We have practically now about 1,000. Your management has in mind plans in regard to the advancement of the Journal to make it still more representative, having it cover wider fields, but for this purpose money is necessary, and money with our present ideas in regard to our present society can only come to us, at least as far as we can see, through increase in membership. Will not every member of the society do something in the next four or five months to increase our membership. We certainly are well established on a good foundation. It is an honor to be a member of our society. We give a full requital for everything we get from our membership, and certainly the time is fast approaching when any American chemist who expects to keep up with his profession cannot afford to be outside of the Society. Let every member bring one member with him and more if possible, at the Troy meeting or bring them in between now and then. I will call upon the Secretary for a few announcements connected with the Society.

The Secretary : Perhaps I might say, Mr. President, that Dr. Mason with becoming modesty has failed to remind you that the oldest institution, if I am not mistaken, for the education of

civil engineers, is in Troy, and as a representative of the institution, he has some modesty in speaking of it. Allow me to call attention to one point in reference to increase in membership; there is provided in the constitution a class of members who are not necessarily chemists, but who are interested in chemistry, the associates; and it would seem as though there might be a large amount of recruiting from this source. There are very many people who do not feel themselves distinctively chemists and yet they are interested either through their business or by their inclination in the development of chemistry; and it would seem possible to have as large a membership of associates as of active members. We can do a good work in that way, and the $5.00 of an associate is worth just as much as the $5.00 of an active member.

In regard to the membership of the society, I would say that last spring, somewhere about March, I think, for the first time in the history of the Society, we struck a membership of a full round 1000 in number. (Applause.)

The President: I am sure those of us who have the pleasure of being at this meeting can not fail to have recognized that there has been at the helm some guiding hands, and I am going to say for your information that those guiding hands are not the officers of the Society but the local committee. I feel that it would be improper for us to close the meeting without some recognition of the kindness we have received at the hands of our members here and also those who have contributed to our happiness during this visit. I will call upon Prof. Mason to propose due recognition.

Prof. Mason: Mr. President and Gentlemen; it seems to me entirely fitting that we should pass a vote of thanks to those who have so kindly looked after our pleasure and interest, and I will therefore move you that the thanks of this society are due to the local committee of arrangements, Drs. H. M. Hill, J. A. Miller, T. B. Carpenter, L. E. Levi, also to the local committee of the American Association for the Advancement of Science, especially Mr. Eben P. Dorr, Secretary, also to the local press and to the managers and directors of the various works visited; namely, the Milsom Rendering and Fertilizing Works, Garbage Reduction

Works, Lang's Brewery, Buffalo Reduction Company, Calcium Carbide Works (Niagara Works), Cataract Construction Company, Cliff Paper Mill, Tonawanda Iron and Steel Company, Schoellkopf Aniline and Chemical Company, Crystal Water Company, also Jaeger's Roof Garden and Café.

The President put the question on the adoption of the motion, which was carried unanimously.

The President: Is there any further information desired or any further question to come up?

Prof. Mason: May I ask this question: Is it possible to so arrange matters as to consolidate the summer meetings of the Chemical Society and Section C? I ask it because I personally can be away but a week. The two meetings occupy more than a week. I should like to attend the two meetings in full, but I can not do it. My position is such that I am obliged to return next Wednesday night. The result is I cut off half nearly of the American Association meeting. Inasmuch as it is a meeting of almost the same men under different names, is it not possible to so arrange matters as to have them all together.

Dr. Norton: I feel very much as Dr. Mason does. In order to bring this to decisive action I move you that the Council be authorized to use its discretion in arranging for a joint meeting of this society and Section C of the American Association next year. I think this will enable us to give an expression to our feelings and leave the Council free to take the proper measures. I know a number of our members are coming on next week. They do not feel as though they could give nine or ten days to the meeting of both societies. There are a number present in the room who will have to leave next Monday or Tuesday. By a little careful study we can arrange to have the whole chemical work that would come before the Society and before Section C of the American Association, carried on in the sessions of the five days which are given up for that purpose. I think it would be much more desirable because we do not want our membership stringing along through some seven days, part of us listening to papers now, and part at the end of the week. I feel from conversation with a number of our members that there is a general belief that we ought to have some simple arrangement for joint

meetings, and they can be presided over alternately by the President of our Society and the vice-president of Section C.

Mr. Prescott: I second the motion, and I think at the present time when the meetings of the Association are as they are, that the plan can be carried out much better than it would have been before the present arrangement had taken place.

Prof. Hart: I second the motion, Mr. President, but I wish to point out one matter that ought to be thought of, that is, the increasing number of papers. We have ten more papers at this meeting than we had last year, and most of you have already received programs of Section C of the American Association and can see what an enormous program that is. People who take the trouble and pains to prepare papers for these meetings naturally feel that they would like to have the papers read. That is a thing to which we should give careful recognition. If anything of the kind is done it is not possible, I think, to secure any more time in Section C than we have now, and according to the printed program that time is already taken up. We have not read more than one-half the papers.

Prof. Kennicott: It does not seem to me it would be a wise thing to sink our identity in any other society. Simply to meet with Section C would seem to me to be loss of identity.

Dr. Hale: Mr. President, it seems to me the motion that has been made is eminently a proper one. The various points one way or the other of difficulty or ease of adjustment would come properly before the Council for consideration and they would have plenty of time to confer with one another and consider the subject. Certain it is that we have a large number of chemists who are increasingly loyal and devoted both to the American Chemical Society and Section C, and by bringing the chemists together at this time we have undoubtedly added to the attendance and the interest and the number of papers of both. It seems to me that the whole subject is wisely referred to the Council of the Society, and of course Section C can take whatever similar action it chooses.

Mr. Breneman: I am quite in accord with the resolution, but it seems to me it would simplify matters very much if we should simply decide to abolish the summer meeting and let the

winter meeting be the only one. That is the annual meeting; i is the meeting where the election occurs and the one of greates interest. I do not see any reason for a joint meeting. If th arrangement suggested is made, the winter meeting will be dis tinctive and the only annual meeting of the society.

Prof. Kennicott: I see that my predictions are to be verified We have already started to sink the identity of the Society. A great many members would be unable to attend any meeting i the winter.

Dr. Prescott: Mr. President, I think the Council would b very glad if we could have a general expression of opinion lik that of Prof. Kennicott and others very briefly at this time.

Dr. Howe: The suggestion that has been made is one I remember when the original discussion took place in regard t the reorganization of the Chemical Society. It was proposed a that time that the American Chemical Society should have it winter meeting, but that the summer meeting should not be fo the reading of papers; that the papers then should be read a the meeting of the American Association. It certainly is not desirable to carry on any merging of identity, at the same time it seems to me that the plan suggested would be a valuable one to those of us who are present here as chemists, and more valuable than the present plan, if we can mass together all the papers and have all the members present in a four days' session, so that we could have the fullest and most helpful discussion. Some of us are unfortunately unable to be present at the winter meeting, but I think even for us it would be better if all the papers were presented together in the meeting of the American Association in the summer. It does not seem to me we want to do anything to injure the American Association or have things in such a situation that we feel obliged to come here this week and go off next week and miss everything that goes on in the Association. I think the Association owes a great deal to the Chemical Society for what it has done in stirring up an interest again in Section C. I think there should be some amicable arrangement of this matter.

Prof. Mason: Just one word I would like to say. We come here, it is true, to listen to chemical papers, but we also come to

meet chemists, and if we have an opportunity of meeting all the members of the American Chemical Society and the members of Section C as well, we fulfil the second object we came for better than if we should string the meeting over so many days, and as a result one man goes before another arrives and perhaps they want to see each other.

Dr. McMurtrie: Mr. Chairman, there are some difficulties that occur to me in this connection. The matter has been of course discussed a good deal during the past three or four or five years; it had been when the reorganization of the Chemical Society occurred, and one of the important difficulties has arisen to my mind during the last year or so when I have been more or less active in the work of Section C of the American Association. In preparing the program of proceedings for last year I was reminded that it was impossible to have papers presented in the meetings of Section C by any other than members of the American Association. Now there is a larger portion of the membership of the American Chemical Society who are not members of Section C. The consolidation of the meetings will necessarily rule out those men from participation in the meeting. This point would of course be brought before the Council in a discussion of the matter, and would, I suppose, have weight. There are a good many members of the Chemical Society, I know, who feel that they do not care to have membership in the American Association, and it seems to me that in any action we take in this regard their wishes should be carefully considered. I think it might be possible to arrange to have the meetings succeed each other in the same week, but that arrangement which has been followed in the past year, has been objected to by the officers of the American Association, holding that it interfered in a large measure with the work of the Association. It was in a measure on this account that the meetings of the Association are fixed for the week continuously; that is beginning with Monday. So that those societies which are called by the officers of the Association, affiliated societies might have their meeting either in the week preceding or succeeding the meeting of the Association. There seems to be a feeling, I think, among a good many of the officers of the Association that it would be in a measure

impossible to secure the coalescence of the different societies with the similar sections. As I say, all these points will be brought necessarily before the Council in the discussion of the matter, and it is the only way in which it can be determined after all. It must, under the constitution, go before the Council before it is open again to be brought before the Society.

Mr. Cochran : Before the question is put I would like to ask one question, and that is this : I myself see some objections to it, but I do want to attain it ; I would like to attend both meetings if I could; I would like to be here when all the chemists are here. This year particularly, my time is very limited ; I shall leave Buffalo this evening and be cut out of the meetings next week entirely. The question I wanted to ask is this : Is it impossible that both meetings should run on at the same time? Could we not have a section meeting or the meeting of the American Chemical Society conducted at the same time that the meeting of Section C of the American Association is conducted? The programs are large. Some of us would desire to hear papers in one section one week and some in the other, and in that way we could save our time and get the papers presented so that we could all hear them. I know there are objections to it, but at the same time I desire to have the subject considered.

Dr. McMurtrie : We are not alone in this matter. Nearly all the other sections of the Association are in about the same position, and it is coming to be a serious question as to what shall be done in this matter, whether the American Association shall be taken into a confederation of scientific societies, or whether some such plan as is suggested now shall be carried out. It seems to me that this might be permitted to grow into a confederation.

The President: I was about to remark on that same subject that there are other affiliated bodies exactly in the same position as Dr. McMurtrie has said, so that it is obvious this question is a serious one.

The President put the question and it was adopted.

Dr. Norton: Mr. President, I would like to say a few words as to what has been said in regard to the pleasure and profit we have all had in meeting together as a Society during the past few days, and I feel that our success, which is actually a marked one this year in point of attendance and interest, is due not only to the efforts of our Local Committee, but also to the able preparation made in advance for the meeting by the officers of the Society, and I would therefore like to move before we separate to-day, that the cordial thanks of the Society be expressed to the President and Secretary for the measures which they have taken to render this meeting so successful, and I would like to ask the Nestor of the Society, Dr. Prescott, to put that motion.

Dr. Prescott: I am very glad to place this motion before you and have an opportunity to vote for it.

Dr. Prescott put the motion which was unanimously carried.

The President: In behalf of the officers, I will only say that it is a regret on their part that most of us are so busy with our daily life that we can not give all that is in our hearts and minds to do for the interests of the Society, and we thank you for your vote. (Applause).

The President: I declare then the meeting adjourned until the Troy meeting.

ANNOUNCEMENT.

All persons who have papers to offer for the next general meeting, which will be held the latter part of December in Troy, N. Y., are requested to forward at their *earliest opportunity* an abstract, or the full manuscript of their papers together with titles and names of authors to the General Secretary, Albert C. Hale, 551 Putnam Ave., Brooklyn, N. Y., so that the papers may all be passed upon by the committee on papers and publications in time for announcement upon the program which must be in print before the meeting.

CHANGES OF ADDRESS.

Burt, M. C., 106 Chestnut St., Springfield, Mass.

Conradson, P. H., Franklin, Pa.

Eakins, L. G., care of Guppenheim Smelting Co., Perth Amboy, N. J.

Lane, Henry M., care of Washington Agricultural College, Pullman, Wash.

Mar, F. W., 32 McDonough St., Brooklyn, N. Y.

McCrae, John, 7 Kirklee Gardens, Kelvinside, Glasgow, Scotland.

Welles, Albert H., 635 Quincy Ave., Scranton, Pa.

Whitehead, Robt. L., Box 142, Mt. Washington, Md.

Issued with November Number, 1896.

Proceedings.

COUNCIL.

By direction of the Council a congratulatory address was forwarded to Stanislas Canizzaro, an honorary member of this Society, upon his seventieth birthday.

December 29 and 30 has been selected as the date for the annual meeting at Troy, N. Y.

MEMBERS ELECTED SEPTEMBER 21, 1896.

Belden, A. W., Chapel Hill, N. C.
Blair, Augustine W., Guilford College, N. C.
Chamot, Emile M., Cornell Univ., Ithaca, N. Y.
Davis, Dr. Floyd, Des Moines, Iowa.
Haller, H. Loft, F.C.S., 27 Hilda St., Beverly Road, Hull, England.
Hotopp, C. H., Stroudsburg, Pa.
Kruskal, Dr. Nicholas, 72 Delancy St., N. Y. City.
Marlatt, Miss Abby L., Providence, R. I.
Meade, Richard K., Longdale, Alleghany Co., Va.
Patrick, George E., Dept. of Agr., Washington, D. C.
Slosson, E. E., Laramie, Wyo.
Smith, Prof. E. G., Beloit College, Beloit, Wis.
Stahl, Dr. Karl F., 57th St. and A. V. R. R., Pittsburg, Pa.
Tolman, Frank L., U. S. Naval Lab., Brooklyn, N. Y.

ASSOCIATE ELECTED SEPTEMBER 21, 1896.

Brinton, C. S., West Chester, Pa.

CHANGES OF ADDRESS.

Bachman, Irving A., Allentown, Pa.
Behr, Arno, 17 Lawn Ridge, Orange, N. J.
Doerflinger, Wm. F., 85 Lafayette Ave., Brooklyn, N. Y.
Boot, J. C., Brooklyn Distilling Co., Kent Ave., Brooklyn, N. Y.
Dal Molin, A. A., 30 E. 18th St., N. Y. City.
Davidson, Geo. H., 28 Woodbine St., Brooklyn, N. Y.
Fuller, Fred. D., Agr. Expt. Sta., Geneva, N. Y.
Habirshaw, William M., Glenwood Works, Yonkers, N. Y.

Hollick, Herbert, Post Office, New York City.
Kutroff, Adolph, 128 Duane St., New York City.
Loeb, Morris, 118 W. 72nd St., New York City.
Munsell, C. E., 110 Horatio St., New York City.
Sargent, Geo. W., Univ. of Pa., Dormitories, 37th and Spı
Sts., Philadelphia, Pa.
Thompson, F., 11 Willmot St., Ann Arbor, Mich.
Tidball, Walton C., 291 Prospect Pl., Brooklyn, N. Y.
Volckening, G. J., 65 Van Buren St., Brooklyn, N. Y.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The first meeting for the year 1896–97 was held at Pr dence, on Thursday evening, September 24th, Chairman E. Pearce presiding.

Prof. J. H. Appleton read a paper upon the "Electrolysis Salt."

The introduction to this paper was a brief discussion of present chemical application of electricity. First in importa at present is the preparation of metals, copper, gold from c nide solutions, zinc, glucinum, and even some more difficu reducible metals or non-metals; sodium, lithium, cadmi cobalt, nickel, and phosphorus. Next, reference was made the production of certain compounds in which primarily heat of the current is involved: silicon carbide, calcium c bide, as well as those metallic carbides, produced by Moiss which, with water, yield such varied hydrocarbons (very s gestive in relation to the origin of petroleum).

The electrolysis of salt by several methods, notably Castne was next taken up.

In conclusion, there were presented some comments on probable influence of the electrolysis of salt on the alkali dustry.

NEW YORK SECTION.—ANNUAL MEETING.

OCTOBER 9, 1896.

The meeting was called to order at 8.20 P. M., by Dr. P. Austen, Chairman.

In the absence of the secretary, Dr. A. C. Hale was appointed secretary *pro tem*.

The minutes of the meeting held June 8th, 1896, were read and approved.

Reports of officers and committees being in order, the chairman called upon Dr. Hale to report for the delegates to the Scientific Alliance of New York. Dr. Hale made a brief oral report, which was accepted.

Dr. P. T. Austen, the retiring chairman of the section, reported on the work of the year and the general condition and prospects of the section and the society as well as the outlook for American chemists generally.

After these remarks by the retiring chairman the election of officers of the section for the ensuing year was held.

Dr. Durand Woodman was unanimously elected secretary and treasurer. Other officers were elected unanimously, as follows :

Chairman—Dr. Wm. McMurtrie.

Executive Committee—Dr. Charles A. Doremus, Prof. A. A. Breneman, Dr. Albert C. Hale.

Delegates to the Scientific Alliance of New York—Dr. Wm. McMurtrie, Dr. C. F. McKenna, Dr. C. A. Doremus.

Dr. Wm. McMurtrie, chairman-elect, then took the chair, and upon motion of Dr. Doremus, a vote of thanks to the retiring chairman was passed unanimously.

Prof. Breneman reported very encouraging progress in reference to the proposed chemical club.

Papers were read and discussed as follows : "Some Disputed Points about the Light of Carbon," by Woodbridge H. Birchmore ; discussed by Prof. Speyers, Mr. Birchmore, and Mr. Stillwell. "The Conversion of Cow Milk into a Substitute for Human Milk," by Henry A. Bunker ; discussed by Dr. Eccles, Dr. Bunker, and Dr. McMurtrie.

Upon motion of Dr. Doremus, seconded by Dr. Squibb, the following named persons were appointed a committee to cooperate with other scientific bodies in New York for the purpose of securing a lecture from Prof. Henri Moissan before his return to

France: C. A. Doremus, A. A. Breneman, M. Loeb, and Wm. McMurtrie.

Upon motion of Dr. Hale, the chairman of the section was authorized and requested to appoint a committee, with himself as chairman, to arrange the programs for the meetings of the section during the year.

The meeting then adjourned.

Issued with December Number, 1896.

Proceedings.

COUNCIL.

At the Buffalo meeting of the American Chemical Society it was voted that the Council be requested to take into consideration ways and means for bringing the Summer meeting of the Society into closer relation with that of Section C of the A. A. A. S., so that both meetings, if possible, may be held within the same week, thus affording the opportunity for all chemists to attend both meetings.

Inasmuch as both these bodies were well represented at the meeting referred to, it was suggested that a good deal of time could be gained by appointing then and there a committee of conference from each. This was accordingly done, the committee on the part of the American Chemical Society being Messrs. W. P. Mason, W. McMurtrie, Edward Hart, T. H. Norton and A. B. Prescott.

A joint meeting of this Committee was held with a Committee of Section C, and the following recommendations were agreed upon:

1st. Section C to have a business meeting for purposes of organization on Monday of the week of meeting, and the Vice-President's address to take place late in the afternoon of that day.

2nd. The American Chemical Society to be given Monday and Tuesday for their work.

3rd. Section C of the A. A. A. S. to be given the balance of the week.

4th. The arrangement of the program for the reading of papers before the two bodies to be left to the discretion of the President of the American Chemical Society and the Vice-President of Section C of the A. A. A. S.

These recommendations were approved by Council Oct. 27, 1896.

In view of the increasing number of papers presented at th meetings, the Council has decided that the Troy meeting sha extend over three days if this shall be found necessary.

NEW MEMBERS ELECTED NOVEMBER 5, 1896.

Andrews, Prof. W. W., Sackville, New Brunswick.
Burner, Prof. N. L., Ohio Med. Univ., Columbus, Ohio.
Case, Wm. A., Mt. Washington, Baltimore Co., Md.
Clark, Arthur W., Conshohocken, Pa.
Evans, Wm. Lloyd, Ohio State Univ., Columbus, O.
Fossler, Miss Mary L., 734 N. 9th St., Lincoln, Nebr.
Hochstetter, Robert W., Oak St. and Bellevue Ave., Cincinnati, O.
Levi, Louis E., Ph.D., 548 Franklin St., Buffalo, N. Y.
Mathews, John Alex., Columbia Univ., N. Y. City.
Mooers, Chas. A., Agr. Exp. Sta., Knoxville, Tenn.
Schoen, Joseph, 2317 Indiana Ave., Chicago, Ill.
Schroeder, J. Henry, Grand and Nassau Sts., Cincinnati, O
Sturcke, H. E., 284 Pearl St., N. Y. City.
Sy, Albert P., Univ. of Buffalo, 24 High St., Buffalo, N. Y
Wessling, Prof. Hannah L., 147 Milton St., Cincinnati, O.

ASSOCIATES ELECTED NOVEMBER 5, 1896.

Cooley, Fred. C., 1029 L St., Lincoln, Nebr.
Culver, Frank S., 1610 K St., Lincoln, Nebr.
Dales, Benton, 1242 P St., Lincoln, Nebr.
Himrod, George, 1446 Q St., Lincoln, Nebr.
Hiltner, Martin E., 1301 N St., Lincoln, Nebr.
Lange, Miss Helen P., 346 N. 17th St., Lincoln, Nebr.
O'Sullivan, Miss Eva, 445 N. 13th St., Lincoln, Nebr.
Pharmelee, Howard C., care of Cooperative Book Co., Lincoln, Nebr.
Thatcher, Roscoe W., 540 N. 15th St., Lincoln Nebr.

CHANGES OF ADDRESS.

Allen, Walter S., 34 So. 6th St., New Bedford, Mass.
Cushman, Allerton S., Chemical Laboratory, Harvard Univ., Cambridge, Mass.
Hancock, David, 1720 Fifth Ave., Birmingham, Ala.
Reese, Chas. L., 1801 Linden Ave., Baltimore, Md.
Sturm, Arthur B., Box 92, Maywood, Ill.

ADDRESS WANTED.

Bradley, Edson, formerly of 35 Broadway, New York City.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

A meeting of the Rhode Island Section was held at Providence, on Thursday evening, October 29, 1896.

Mr. E. D. Pearce mentioned the results of his experiments in bleaching brown tower acid. Samples of acid taken before and after bleaching were exhibited. Mr. Pearce also stated that the coloring matter of the anthers of the wild evening primrose was altered by acids and alkalies in the same way as turmeric.

A paper was read by W. M. Saunders upon "The Determination of Sulphur in Iron." The reader described briefly the deleterious effect of sulphur in iron. The small amount permitted in foundry work, and the difficulty of determining this amount was mentioned.

Next a description of methods of analysis was given. The reader considered the evolution methods, although not in every case giving the full sulphur contents of the iron, to be accurate enough for practical purposes. The results compare favorably with the oxidation method.

NEW YORK SECTION.

The November meeting of the New York Section was held on the 6th, Professor McMurtrie in the chair, and fifty-one members present.

The chair announced the acceptance by the executive committee of an invitation from Drs. Morton and Leeds to hold the December meeting at the Stevens Institute of Technology.

The death of Mr. Alfred H. Mason was announced and a sketch of his life was read.

A motion was made and seconded that the executive committee be recommended to authorize the secretary to employ a stenographer to report the discussions of papers presented at the meetings; such report, when properly edited, to be sent to the committee on papers, for publication in the Journal.

The following papers were read:

"The Volumetric Determination of Acetone," by Dr. E. R Squibb.

"Notes on a Chemist's Trip Abroad," by C. A. Doremus.

"A New Form of Pyknometer," by J. C. Boot.

"Improvements in the Colorimetric Tests for Copper," b Geo. L. Heath.

"Note on Solubility of Bismuth Sulphide in Alkaline Sul phides," by Geo. C. Stone.

The meeting then adjourned.

CINCINNATI SECTION.

The meeting was held on November 17, in the Lloyd Library After welcoming the Society, Prof. J. U. Lloyd read a paper entitled "Bibliography of American Pharmacy," giving a concise history of the different editions of the U. S. Pharmacopeia and its commentaries, the various dispensatories and formularies. This paper was rendered doubly interesting by the exhibition of the rare old editions of these works from the well-filled shelves of the Lloyd Library. Prof. O. W. Martin read a paper opening the discussion on the "Teaching of Elementary Chemistry." A contribution on this subject by Dr. James Lewis Howe was read by Mr. H. B. Foote. Excerpts from paper which Prof. Paul Freer presented at the summer meeting of American Association for the Advancement of Science, elicited considerable discussion by Dr. Springer, Profs. Norton, Martin and Homburg.

Dr. William H. Crane, of Cincinnati was elected a member of the Section.